

Electromechanical hysteresis and coexistent states in dielectric elastomers

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When a voltage is applied to a layer of a dielectric elastomer, the layer reduces in thickness and expands in area. A recent experiment has shown that the homogeneous deformation of the layer can be unstable, giving way to an inhomogeneous deformation, such that regions of two kinds coexist in the layer, one being flat and the other wrinkled. To analyze this instability, we construct for a class of model materials, which we call ideal dielectric elastomers, a free-energy function comprising contributions from stretching and polarizing. We show that the free-energy function is typically nonconvex, causing the elastomer to undergo a discontinuous transition from a thick state to a thin state. When the two states coexist in the elastomer, a region of the thin state has a large area and wrinkles when constrained by nearby regions of the thick state. We show that an elastomer described by the Gaussian statistics cannot stabilize the thin state, but a stiffening elastomer near the extension limit can. We further show that the instability can be tuned by the density of cross-links and the state of stress.

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I. INTRODUCTION

Soft active materials are being developed to mimic a salient feature of life: movement in response to stimuli.^{1–6} This paper focuses on a family of materials known as dielectric elastomers. Figure 1 illustrates a thin layer of a dielectric elastomer sandwiched between two compliant electrodes. When a voltage is applied between the two electrodes, the dielectric elastomer reduces in thickness and expands in area, causing a weight to move. This phenomenon has been studied intensely in recent years,^{2,5,7–17} with possible applications in medical devices, energy harvesters, and space robotics.^{1,6,18–23}

The dielectric elastomer is susceptible to a mode of failure known as pull-in instability. As the electric field increases, the elastomer thins down, so that the same voltage will induce an even higher electric field. The positive feedback may cause the elastomer to thin down drastically, resulting in an even larger electric field. This electromechanical instability can be a precursor of electrical breakdown, and has long been recognized in the power industry as a failure mode of polymer insulators.^{24,25} The instability has also been analyzed recently in the context of dielectric elastomer actuators.^{10,14,26,27}

In a recent study of the pull-in instability, it was observed experimentally that when a layer of a dielectric elastomer is subject to a voltage, the homogeneous deformation can be unstable, giving way to an inhomogeneous deformation, such that two regions coexist in the layer, one being flat and the other wrinkled.¹⁰ The underlying cause of this behavior has not been discussed in the literature. Here, we develop a theory to show how a homogenous deformation in the dielectric layer can give way to two coexistent states.

Our theory will suggest the following qualitative picture. Figure 2 sketches the relation between the voltage applied between the two electrodes, Φ , and the magnitude of the electric charge on either electrode, Q . When the charge is small, the voltage needed to maintain the charge increases with the charge. This behavior is the same as for any capacitor, and the slope of the voltage-charge curve gives the ca-

pacitance. When the charge is large enough, the elastomer thins down appreciably, and the electric field in the layer is very high, so that the voltage needed to maintain the charge starts to decrease. Consequently, the voltage reaches a peak, which has long been identified with the onset of the pull-in instability.²⁸ The elastomer consists of long-chained polymers cross-linked into a three-dimensional network. Under no load, the end-to-end distance of each polymer chain is small compared to its fully stretched length, known as the *extension limit*. When the elastomer is subject to a large voltage, the polymer chains approach the extension limit, so that the elastomer stiffens sharply, and the voltage increases again with the charge.

The shape of the voltage-charge curve in Fig. 2 underlies a discontinuous transition of the elastomer from a thick state to a thin state. If the voltage is controlled, the elastomer may exhibit hysteresis, jumping from one state to the other, much like a ferroelectric. If the charge is controlled, the two states may coexist in the elastomer at a constant voltage, with the new state growing at the expense of the old. A region of the

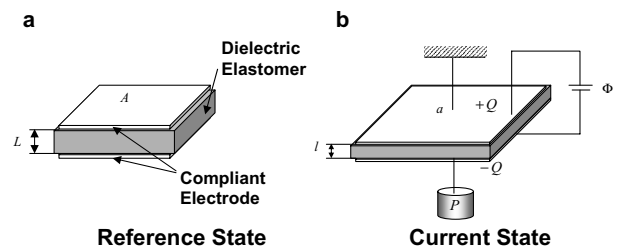


FIG. 1. A thin layer of a dielectric elastomer sandwiched between two compliant electrodes, and loaded by a battery and a weight. (a) In the undeformed reference state, the elastomer has thickness L and area A . (b) In the current state, the battery applies voltage Φ and the weight applies force P . The loads are so arranged that the elastomer deforms homogeneously to thickness l and area a , while an amount of electric charge Q flows via the battery from one electrode to the other. The electrodes are so compliant that they do not constrain the deformation of the elastomer. In practice, the weight may be used to compress the elastomer or to stretch the elastomer in the plane.

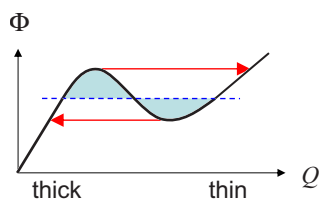


FIG. 2. (Color online) A schematic of the voltage-charge curve of a layer of an elastomer dielectric. When Q is small, Φ increases with Q . When Q is large enough, the layer thins down appreciably, so that the true electric field in the layer is large, and Φ needed to maintain the charge drops. When Q is very large, the layer thins so much that the elastomer becomes very stiff, so that Φ increases with Q .

thin state has a large area and wrinkles when constrained by nearby regions of the thick state. Maxwell's rule in the theory of phase transition applies: The voltage for coexistent states is at the level such that the two shaded regions in Fig. 2 have equal areas.

The need to analyze large deformation of soft materials under diverse stimuli has led us to reexamine the theory of elastic dielectrics. In his classic text, Maxwell²⁹ showed that electric forces between conductors in a vacuum could be calculated by invoking a field of stress in the vacuum. His derivation is outlined in the Appendix of this paper for ease of reference. The Maxwell stress has since been used in deformable dielectrics.^{5,7,30–34} This practice has been on an insecure theoretical foundation. Feynman *et al.*³⁵ remarked that differentiating electrical and mechanical forces inside a solid was an unsolved problem and was probably unnecessary. Recently, we and others have revisited the theory of deformable dielectrics,^{36–38} showing that the Maxwell stress is not applicable to deformable dielectrics in general and that the effect of electric field on deformation is material specific.

The plan of this paper is as follows. Section II outlines the theory of deformable dielectrics. The field equations are applicable for arbitrarily large deformation and are linear partial differential equations. On the basis of available experimental observations, we construct in Sec. III a free-energy function for a class of model materials, which we call ideal dielectric elastomers. The free energy of the elastomer comes from two processes: stretching and polarizing. The polarizing process is taken to be the same as that in a liquid, unaffected by the stretching process. We show that for this special class of materials, the Maxwell stress emerges from the free-energy function. Section IV applies the theory to analyze a layer of a dielectric elastomer deforming under a voltage. We show that an elastomer characterized by the Gaussian statistics cannot stabilize the thin state; to do so, we have to invoke stiffening near the extension limit, as described by non-Gaussian statistics.

II. FIELD EQUATIONS OF DEFORMABLE DIELECTRICS

As a preparation for the later sections, this section summarizes basic equations of the field theory of deformable dielectrics. Following closely the approach of Ref. 27, we express the theory in terms of material coordinates and nomi-

nal quantities, and we do not invoke the notions of electric body force and Maxwell stress. Because a field may also exist in the vacuum surrounding the dielectric, we will regard the vacuum as a special dielectric, with a constant permittivity and vanishing mechanical stiffness. Thus, the field extends to the entire space, both the solid dielectric and the vacuum. All the volume integrals extend over the entire space, and the surface integrals extend over all the interfaces. We take the continuum at a particular time as a reference state and name each material particle using its coordinate \mathbf{X} in the reference state. Let $dV(\mathbf{X})$ be an element of volume and $N_K(\mathbf{X})dA(\mathbf{X})$ be an element of an interface, where $dA(\mathbf{X})$ is the area of the element and $N_K(\mathbf{X})$ is the unit vector normal to the interface between two materials labeled as $-$ and $+$, pointing toward material $+$.

In a current state at time t , a particle \mathbf{X} occupies a place with coordinate $\mathbf{x}(\mathbf{X}, t)$. Denote the deformation gradient by

$$F_{iK} = \frac{\partial x_i(\mathbf{X}, t)}{\partial X_K}. \quad (1)$$

The deformation gradient is a second-rank tensor, and it generalizes the stretches.

We will use the word “weight” as a shorthand for any mechanism that applies an external force to the continuum. Imagine that we hang a weight to each material particle. In the current state, let the force due to the field of weights on an element of volume be $\mathbf{B}(\mathbf{X}, t)dV(\mathbf{X})$ and that on an element of an interface be $\mathbf{T}(\mathbf{X}, t)dA(\mathbf{X})$. Define the nominal stress $s_{iK}(\mathbf{X}, t)$ such that the equation

$$\int s_{iK} \frac{\partial \xi_i}{\partial X_K} dV = \int B_i \xi_i dV + \int T_i \xi_i dA \quad (2)$$

holds true for any test function $\xi_i(\mathbf{X})$.

Applying the divergence theorem, we obtain

$$\int s_{iK} \frac{\partial \xi_i}{\partial X_K} dV = \int (s_{iK}^- - s_{iK}^+) N_K \xi_i dA - \int \frac{\partial s_{iK}}{\partial X_K} \xi_i dV. \quad (3)$$

Across the interface, $\xi_i(\mathbf{X})$ is assumed to be continuous, but the stress need not be continuous. Insisting that Eq. (2) holds true for any test function $\xi_i(\mathbf{X})$, we find that the nominal stress obeys

$$\frac{\partial s_{iK}(\mathbf{X}, t)}{\partial X_K} + B_i(\mathbf{X}, t) = 0 \quad (4)$$

in the volume and

$$[s_{iK}^-(\mathbf{X}, t) - s_{iK}^+(\mathbf{X}, t)] N_K(\mathbf{X}, t) = T_i(\mathbf{X}, t) \quad (5)$$

on an interface. Equations (4) and (5) express momentum balance in every current state in terms of the nominal fields. While these equations are well known in continuum mechanics, we should emphasize that \mathbf{B} and \mathbf{T} are forces associated with the field of weights; the notion of electrical body forces need not be invoked in the theory of deformable dielectrics.

We will use the word “battery” as a shorthand for any mechanism that applies an electric voltage to a material particle. Imagine that we attach a battery to every material particle. In the current state, the battery maintains the voltage of

the particle, $\Phi(\mathbf{X}, t)$, with respect to the ground. Denote the nominal electric field as the gradient of the electric potential,

$$\tilde{E}_K = - \frac{\partial \Phi(\mathbf{X}, t)}{\partial X_K}. \quad (6)$$

The negative sign conforms to the convention that the electric field points from a particle with high electric potential to a particle with low electric potential.

In the current state, let the charge on an element of volume be $Q(\mathbf{X}, t)dV(\mathbf{X})$ and the charge on an element of an interface be $\Omega(\mathbf{X}, t)dA(\mathbf{X})$. Define the nominal electric displacement $\tilde{D}_K(\mathbf{X}, t)$ such that

$$\int \left(- \frac{\partial \eta}{\partial X_K} \right) \tilde{D}_K dV = \int \eta Q dV + \int \eta \Omega dA \quad (7)$$

holds true for any test function $\eta(\mathbf{X})$.

We apply the divergence theorem to the left-hand side and obtain

$$\int \frac{\partial \eta}{\partial X_K} \tilde{D}_K dV = \int \eta (\tilde{D}_K^- - \tilde{D}_K^+) N_K dA - \int \eta \frac{\partial \tilde{D}_K}{\partial X_K} dV. \quad (8)$$

The test function $\eta(\mathbf{X})$ is assumed to be continuous across the interface, but the electric displacement need not be continuous across the interface. Insisting that Eq. (7) holds true for any test function $\eta(\mathbf{X})$, we find that the nominal electric displacement obeys

$$\frac{\partial \tilde{D}_K(\mathbf{X}, t)}{\partial X_K} = Q(\mathbf{X}, t) \quad (9)$$

in the volume and

$$[\tilde{D}_K^+(\mathbf{X}, t) - \tilde{D}_K^-(\mathbf{X}, t)] N_K(\mathbf{X}, t) = \Omega(\mathbf{X}, t) \quad (10)$$

on an interface. These equations express Gauss's law in every current state in terms of the nominal fields.

In the above, we have used nominal quantities exclusively. For later reference, recall the well known relations between the true and nominal quantities. The true stress σ_{ij} relates to the nominal stress by

$$\sigma_{ij} = \frac{F_{jK}}{\det(\mathbf{F})} s_{iK}. \quad (11)$$

The true electric displacement relates to the nominal electric displacement by

$$D_i = \frac{F_{iK}}{\det(\mathbf{F})} \tilde{D}_K. \quad (12)$$

The true electric field relates to the nominal electric field by

$$E_i = H_{iK} \tilde{E}_K, \quad (13)$$

where H_{iK} is the inverse of the deformation gradient, namely, $H_{iK} F_{iL} = \delta_{KL}$ and $H_{iK} F_{jK} = \delta_{ij}$.

III. IDEAL DIELECTRIC ELASTOMERS

The field equations [Eqs. (1), (4), (6), and (9)] are linear partial differential equations; they determine the field in con-

junction with material laws, which we specify in this section. When the material particles displace by $\delta \mathbf{x}$, the weights do work, $\int B_i \delta x_i dV + \int T_i \delta x_i dA$. When small amount of charge δQ and $\delta \Omega$ flows from the ground to the material particles, the batteries do work, $\int \Phi \delta Q dV + \int \Phi \delta \Omega dA$.

Let the free energy of the dielectric per unit reference volume be W , taken to be a function of the deformation gradient and the nominal electric displacement, $W(\mathbf{F}, \tilde{\mathbf{D}})$. Associated with small changes $\delta \mathbf{F}$ and $\delta \tilde{\mathbf{D}}$, the free energy changes by

$$\delta W = \frac{\partial W(\mathbf{F}, \tilde{\mathbf{D}})}{\partial F_{iK}} \delta F_{iK} + \frac{\partial W(\mathbf{F}, \tilde{\mathbf{D}})}{\partial \tilde{D}_K} \delta \tilde{D}_K. \quad (14)$$

The dielectric, the weights, and the batteries together form a thermodynamic system. The free energy of the system, G , is a sum of the free energy of the dielectric and the potential energy of the weights and batteries. Consequently, associated with the small changes, the free energy of the system changes by

$$\begin{aligned} \delta G = & \int \delta W dV - \int B_i \delta x_i dV - \int T_i \delta x_i dA - \int \Phi \delta Q dV \\ & - \int \Phi \delta \Omega dA. \end{aligned} \quad (15)$$

Applying Eqs. (14), (2), and (7) to Eq. (15), we obtain

$$\delta G = \int \left(\frac{\partial W}{\partial F_{iK}} - s_{iK} \right) \delta F_{iK} dV + \int \left(\frac{\partial W}{\partial \tilde{D}_K} - \tilde{E}_K \right) \delta \tilde{D}_K dV. \quad (16)$$

Thermodynamics dictates that an equilibrium state minimizes the free energy of the system. That is, $\delta G = 0$ for any small changes, $\delta \mathbf{F}$ and $\delta \tilde{\mathbf{D}}$, in the neighborhood of the equilibrium state. Consequently, the coefficients in front of the two variations must vanish, leading to

$$s_{iK} = \frac{\partial W(\mathbf{F}, \tilde{\mathbf{D}})}{\partial F_{iK}}, \quad (17)$$

$$\tilde{E}_K = \frac{\partial W(\mathbf{F}, \tilde{\mathbf{D}})}{\partial \tilde{D}_K}. \quad (18)$$

Once the function $W(\mathbf{F}, \tilde{\mathbf{D}})$ is known for an elastic dielectric, Eqs. (17) and (18) give material laws.

The free-energy density $W(\mathbf{F}, \tilde{\mathbf{D}})$ is a function of a tensor and a vector. An explicit form of such generality is unavailable for any real material. On the other hand, experiments suggest that for dielectric elastomers, the true electric displacement is linear in the true electric field, $D = \epsilon E$, with the permittivity ϵ being approximately independent of the state of deformation.^{5,7,9,10} We interpret this experimental observation as follows. Each polymer in an elastomer is a long chain of covalently bonded links. The neighboring links along the chain can readily rotate relative to each other, so that the chain is flexible. A link also interacts with links on other

chains through weak bonds. Different chains are cross-linked with covalent bonds to form a three-dimensional network. When each chain contains a large number of links and when the end-to-end distance of the chain has not reached its fully stretched length, the extension limit, the local behavior of the links is just like molecules in a liquid. The elastomer can polarize nearly as freely as in liquids. Furthermore, for an elastomer with an approximately isotropic dielectric behavior, we surmise that the polarizability of links is comparable in the directions along the chain and transverse to the chain.

Motivated by the experimental observation and molecular interpretation, we define an *ideal dielectric elastomer* such that its free energy is the sum of the free energy due to stretching the network and the free energy due to polarizing the liquid polymer. We will take unstretched, unpolarized elastomer as the reference state. The free energy of the liquid polymer per unit current volume is $D_i D_i / 2\epsilon$. Thus, the free-energy function of the ideal dielectric elastomer is

$$W(\mathbf{F}, \tilde{\mathbf{D}}) = W_s(\mathbf{F}) + \frac{F_{iK} F_{iL}}{2\epsilon \det(\mathbf{F})} \tilde{D}_K \tilde{D}_L. \quad (19)$$

The term $W_s(\mathbf{F})$ is the free energy due to stretching the three-dimensional network. We assume that the free energy of stretching is mainly due to the entropy of the flexible chains, and neglect any effect of electric field on the free energy of stretching.

Inserting Eq. (19) into Eq. (18), we obtain

$$\tilde{E}_K = \frac{F_{iK} F_{iL}}{\epsilon \det(\mathbf{F})} \tilde{D}_L, \quad (20)$$

which reduces to $D_i = \epsilon E_i$. As anticipated, the dielectric behavior of the ideal dielectric elastomer is identical to that of a liquid polymer.

Inserting Eq. (19) into (17), and recalling an identity $\partial \det(\mathbf{F}) / \partial F_{iK} = H_{iK} \det(\mathbf{F})$, we obtain

$$s_{iK} = \frac{\partial W_s(\mathbf{F})}{\partial F_{iK}} + \frac{F_{iL} \tilde{D}_L \tilde{D}_K}{\epsilon \det(\mathbf{F})} - \frac{F_{kL} F_{kM} H_{iK} \tilde{D}_L \tilde{D}_M}{2\epsilon \det(\mathbf{F})}. \quad (21)$$

Using Eqs. (11), (12), (23), and (20), we reduce Eq. (21) to

$$\sigma_{ij} = \frac{F_{jK}}{\det(\mathbf{F})} \frac{\partial W_s(\mathbf{F})}{\partial F_{iK}} + \epsilon E_i E_j - \frac{\epsilon}{2} E_k E_k \delta_{ij}. \quad (22)$$

The first term is due to stretching the network, and the second and third terms are due to the electric field.

A comparison of Eq. (22) with the Appendix shows that the electric field induced stress in an ideal dielectric elastomer takes the same form as the Maxwell stress in a liquid. This relation is not accidental because we have modeled the dielectric behavior of the elastomer after a liquid. For a general solid dielectric, however, the free-energy function does not take the form of Eq. (19), so that the effect of electric field on stress will not take the form of the Maxwell stress. For example, when a solid dielectric is subject to a voltage, the layer will become thinner or thicker, depending on the dielectric used.³⁹⁻⁴² For a dielectric that thickens under an electric field, the Maxwell stress does not even predict the correct sign of the strain. The atomic origin of this thicken-

ing is well understood. Influenced by the voltage between the electrodes, charged particles inside the dielectric tend to displace relative to one another, often accompanied by an elongation of the material in the direction of the electric field. In the literature, when the strain induced by an electric field in a dielectric deviates from that predicted by the Maxwell stress, the strain is called electrostriction. Effort has even been made to differentiate electrostriction from the strain induced by the Maxwell stress. Within our theory, however, the Maxwell stress has lost its significance for general dielectrics. This is particularly true when the dielectric behavior is nonlinear, or when the permittivity depends on deformation, so that the Maxwell stress is not even defined. In general, once the free-energy function is prescribed, Eqs. (17) and (18) give the complete material laws.

By definition (7), the nominal electric displacement field $\tilde{\mathbf{D}}$ is invariant when the entire system in the current state rotates as a rigid body. The deformation gradient \mathbf{F} , however, varies when the system in the current state rotates as a rigid body. To ensure that the free energy is invariant under such a rigid-body rotation, following the usual practice, we invoke the right Cauchy-Green deformation tensor, $C_{KL} = F_{iK} F_{iL}$, and write the free energy as a function, $W = W(\mathbf{C}, \tilde{\mathbf{D}})$. Consequently, Eq. (17) becomes

$$s_{iK} = 2F_{iL} \frac{\partial W(\mathbf{C}, \tilde{\mathbf{D}})}{\partial C_{KL}}. \quad (23)$$

Under most types of load, an elastomer can undergo large shape change without appreciable volumetric change. Following the common practice, we assume that the elastomer is incompressible, so that

$$\det(\mathbf{F}) = 1. \quad (24)$$

In minimizing the free energy G , the condition of incompressibility can be enforced as a constraint by adding $\int p[1 - \det(\mathbf{F})]dV$ to G , where $p(\mathbf{X}, t)$ is a field of Lagrangian multipliers. Subject to the condition of incompressibility, Eq. (17) becomes

$$s_{iK} = 2F_{iL} \frac{\partial W(\mathbf{C}, \tilde{\mathbf{D}})}{\partial C_{KL}} - p H_{iK} \quad (25)$$

and Eq. (22) becomes

$$\sigma_{ij} = 2F_{jK} F_{jL} \frac{\partial W_s(\mathbf{C})}{\partial C_{KL}} - p \delta_{ij} + \epsilon E_i E_j - \frac{\epsilon}{2} E_k E_k \delta_{ij}. \quad (26)$$

The true stress is a symmetric tensor, and p corresponds to a state of hydrostatic stress.

Many forms of $W_s(\mathbf{C})$ can be found in the literature on elastomers.^{43,44} We adopt an expression developed by Arruda and Boyce⁴⁵

$$W_s(\mathbf{C}) = \mu \left[\frac{1}{2}(I - 3) + \frac{1}{20n}(I^2 - 9) + \frac{11}{1050n^2}(I^3 - 27) + \dots \right], \quad (27)$$

where μ is the small-strain shear modulus, $I = C_{KK}$, and n is the number of links per chain. When $n \rightarrow \infty$, Eq. (27) reduces

to the Neo-Hookean law, which is derived from the Gaussian statistics, assuming that the end-to-end distance of a chain is small compared to the length of the fully stretched chain. When the end-to-end distance approaches the length of the fully stretched chain, however, the Gaussian statistics is no longer applicable, and Eq. (27) provides one form of non-Gaussian correction. As the chains approach to being fully stretched, the elastomer stiffens. As we will show below, this stiffening plays an essential role in stabilizing coexistent states.

IV. COEXISTENT STATES

We next apply the general theory to analyze an elastomer layer subject to a weight and a voltage (Fig. 1). The undeformed elastomer is taken to be the reference state, in which the layer has thickness L and area A . In the current state, a weight applies a force P to the layer, while through an external circuit a battery applies a voltage Φ between the two electrodes. The thickness of the layer becomes l and the area becomes a . An amount of charge Q flows from the external circuit from one electrode to the other. Define the stretch by $\lambda=l/L$, the nominal stress by $s=P/A$, the nominal electric field by $\tilde{E}=\Phi/L$, and the nominal electric displacement by $\tilde{D}=Q/A$. These definitions are the special forms of those in Sec. II. The true electric field is defined as $E=\Phi/l$, and the true electric displacement is defined as $D=Q/a$. For incompressible materials, $AL=al$, so that $E=\tilde{E}/\lambda$ and $D=\lambda\tilde{D}$. Observe that in the absence of weight, $s=0$, regardless of whether the dielectric thins or thickens under the voltage.

Let $W(\lambda, \tilde{D})$ be the free-energy function of the elastomer in the current state divided by the volume of the elastomer in the reference state. At constant P and Φ , the potential energy of the weight and the battery are, respectively, $-Pl$ and $-\Phi Q$. The elastomer, the weight, and the battery together constitute a thermodynamic system. The free energy of the system is the sum over the parts, namely,

$$G = LAW(\lambda, \tilde{D}) - Pl - \Phi Q. \quad (28)$$

A state of the system is described by two generalized coordinates, λ and \tilde{D} . We fix both P and Φ , and vary λ and \tilde{D} . Thermodynamics dictates that when the elastomer equilibrates with the weight and the battery, the values of λ and \tilde{D} should minimize the free energy of the system, G .

When the system changes from a state (λ, \tilde{D}) to a state $(\lambda + \delta\lambda, \tilde{D} + \delta\tilde{D})$, the free energy changes by

$$\begin{aligned} \frac{\delta G}{LA} = & \left(\frac{\partial W}{\partial \lambda} - s \right) \delta\lambda + \left(\frac{\partial W}{\partial \tilde{D}} - \tilde{E} \right) \delta\tilde{D} + \frac{\partial^2 W}{2\partial\lambda^2} (\delta\lambda)^2 \\ & + \frac{\partial^2 W}{2\partial\tilde{D}^2} (\delta\tilde{D})^2 + \frac{\partial^2 W}{\partial\lambda\partial\tilde{D}} \delta\lambda \delta\tilde{D}. \end{aligned} \quad (29)$$

This is the Taylor expansion to the second order in $\delta\lambda$ and $\delta\tilde{D}$. For the state (λ, \tilde{D}) to minimize G , the coefficient of the first-order variation must vanish, so that

$$s = \frac{\partial W(\lambda, \tilde{D})}{\partial \lambda}, \quad \tilde{E} = \frac{\partial W(\lambda, \tilde{D})}{\partial \tilde{D}}. \quad (30)$$

Furthermore, the second-order variation must be positive for arbitrary variations $\delta\lambda$ and $\delta\tilde{D}$, so that

$$\frac{\partial^2 W}{\partial\lambda^2} > 0, \quad \frac{\partial^2 W}{\partial\tilde{D}^2} > 0, \quad \left(\frac{\partial^2 W}{\partial\lambda^2} \right) \left(\frac{\partial^2 W}{\partial\tilde{D}^2} \right) > \left(\frac{\partial^2 W}{\partial\lambda\partial\tilde{D}} \right)^2. \quad (31)$$

Conditions (30) are anticipated because the nominal stress is work conjugate to the stretch and the nominal electric field is work conjugate to the nominal electric displacement. Both Eqs. (30) and (31) have familiar graphical interpretations. The function $W(\lambda, \tilde{D})$ is a surface in the space spanned by the coordinates W , λ , and \tilde{D} . Thus, s and \tilde{E} are the slopes of the plane tangent to the surface at (λ, \tilde{D}) . Conditions (31) guarantee that the surface $W(\lambda, \tilde{D})$ is convex at (λ, \tilde{D}) . Of the three conditions in Eq. (31), the first ensures mechanical stability, the second electrical stability, and the third electromechanical stability. As we will see, for typical dielectric elastomers, the first two conditions are satisfied for all values of (λ, \tilde{D}) , but the third is violated for some values of (λ, \tilde{D}) .

In deriving Eq. (30), we have regarded (s, \tilde{E}) as the loading parameters set by the weight and the battery. We may also regard (s, \tilde{E}) as functions of the generalized coordinates (λ, \tilde{D}) . Thus, once the free-energy function $W(\lambda, \tilde{D})$ is prescribed, Eq. (30) gives the equations of state of the elastomer. When the generalized coordinates vary by small amounts, $(\delta\lambda, \delta\tilde{D})$, to maintain equilibrium, Eq. (30) dictates that the loading parameters vary by $(\delta s, \delta\tilde{E})$, such that

$$\begin{bmatrix} \delta s \\ \delta\tilde{E} \end{bmatrix} = \begin{bmatrix} \frac{\partial^2 W}{\partial\lambda^2} & \frac{\partial^2 W}{\partial\lambda\partial\tilde{D}} \\ \frac{\partial^2 W}{\partial\lambda\partial\tilde{D}} & \frac{\partial^2 W}{\partial\tilde{D}^2} \end{bmatrix} \begin{bmatrix} \delta\lambda \\ \delta\tilde{D} \end{bmatrix}. \quad (32)$$

The matrix in Eq. (32), known as the Hessian, linearly maps the changes in the generalized coordinates to the changes in the loading parameters. That is, the Hessian is the generalized tangent modulus.

Before we turn to the specific material model, we first outline consequences of a nonconvex free energy. Figure 3 sketches the behavior of an elastomer loaded with a battery ($\tilde{E} \neq 0$) but not a weight ($s=0$). Assuming mechanical stability, namely, $\partial^2 W(\lambda, \tilde{D})/\partial\lambda^2 > 0$, we conclude that $\partial W(\lambda, \tilde{D})/\partial\lambda$ is a monotonically increasing function, so that the condition $s = \partial W(\lambda, \tilde{D})/\partial\lambda = 0$ can be inverted to express λ as a function of \tilde{D} . This function is sketched in Fig. 3(a): The elastomer thins down as the charge on either electrode increases.

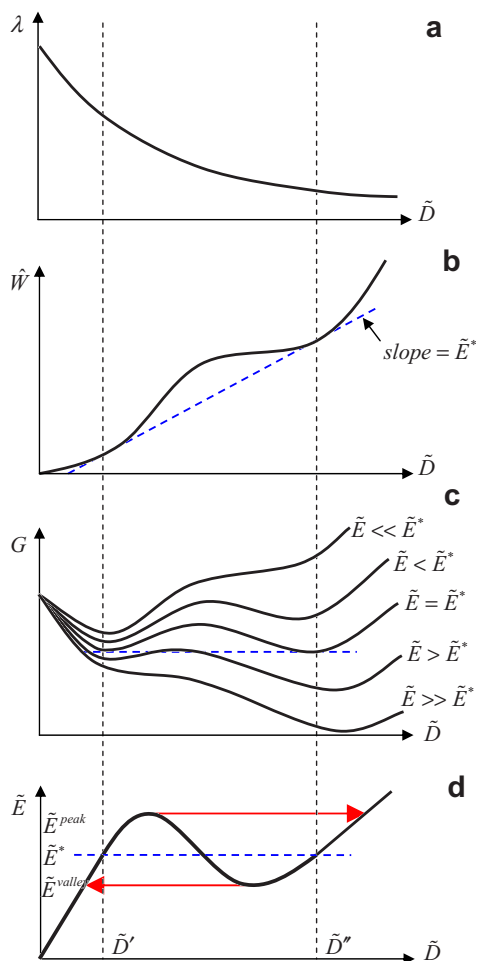


FIG. 3. (Color online) Schematic behavior of a dielectric elastomer under a constant force and variable voltage. All horizontal axes are the nominal electric displacement $\tilde{D}=Q/A$. (a) As the charge increases, the thickness of the electrode reduces. (b) The free-energy function $\hat{W}(\tilde{D})$ is nonconvex. The two states on the common tangent may coexist at the electric field \tilde{E}^* given by the slope of the common tangent. (c) The free-energy function of the composite system of the elastomer and the battery, $G/LA=\hat{W}(\tilde{D})-\tilde{E}\tilde{D}$, where $\tilde{E}=\Phi/L$ is the nominal electric field, i.e., the voltage in the current state divided by the thickness of the elastomer in the reference state. For a small or a large \tilde{E} , the free-energy function has a single minimum, corresponding to a stable equilibrium state. For an intermediate \tilde{E} , the free-energy function has two minima, the lower one corresponding to a stable equilibrium state, and the higher one a metastable equilibrium state. At \tilde{E}^* , the two minima have the equal height, corresponding to the two coexisting states. (d) The function $\tilde{E}(\tilde{D})$ is not monotonic. A voltage-controlled load will result in a hysteresis loop. A charge-controlled load will result in coexisting states, fixing \tilde{E}^* at a level such that the two shaded regions have the same area.

Inserting the relation $\lambda(\tilde{D})$ into the function $W(\lambda, \tilde{D})$, we obtain the free energy of the elastomer as a function of the nominal electric displacement, $\hat{W}(\tilde{D})=W(\lambda(\tilde{D}), \tilde{D})$. This free-energy function is sketched in Fig. 3(b); the function is

convex for small and large \tilde{D} , but is nonconvex for an intermediate range of \tilde{D} . The physical origin of this nonconvex shape has been discussed in connection with Fig. 2.

Figure 3(c) sketches the free energy of the composite system of the elastomer and the battery,

$$G/LA = \hat{W}(\tilde{D}) - \tilde{E}\tilde{D}. \quad (33)$$

Each curve corresponds to a nominal electric field, $\tilde{E}=\Phi/L$. For a small or a large \tilde{E} , the free-energy function has a single minimum, corresponding to a stable equilibrium state. For an intermediate range of \tilde{E} , the function has two minima, with the lower one corresponding to a stable equilibrium state, and the higher one a metastable equilibrium state. At a particular nominal electric field \tilde{E}^* , the two minima have equal values of the free energy. The significance of \tilde{E}^* is understood as follows. Suppose that the state of the elastomer is no longer homogenous, but is composed of two states. The material of the two states occupies areas A' and A'' when undeformed. In this simplified treatment, we will neglect the transition region in the elastomer between the areas of the two states, so that the total area in the reference state is

$$A' + A'' = A. \quad (34)$$

Similarly, the electric charge on one of the electrode is

$$A'\tilde{D}' + A''\tilde{D}'' = Q, \quad (35)$$

and the free energy of the composite system of the elastomer and the battery is

$$G = LA'\hat{W}(\tilde{D}') + LA''\hat{W}(\tilde{D}'') - \Phi(A'\tilde{D}' + A''\tilde{D}''). \quad (36)$$

Thermodynamics requires that in equilibrium this free energy be minimized subject to the constraint $A' + A'' = A$. Setting $\partial G/\partial \tilde{D}' = \partial G/\partial \tilde{D}'' = 0$ and $\partial G/\partial A' = 0$, we obtain

$$\frac{\Phi}{L} = \frac{d\hat{W}}{d\tilde{D}'} = \frac{d\hat{W}}{d\tilde{D}''} = \frac{\hat{W}(\tilde{D}'') - \hat{W}(\tilde{D}')}{\tilde{D}'' - \tilde{D}'}. \quad (37)$$

These conditions have the familiar graphical interpretations. The two states equilibrate when they lie on the common tangent line in Fig. 3(b) or, equivalently, when the two minima have the same height in Fig. 3(c). The slope of the common tangent gives \tilde{E}^* , the nominal electric field under which the two states coexist in equilibrium.

Figure 3(d) sketches the nominal electric field $\tilde{E} = d\hat{W}/d\tilde{D}$ as the function of the nominal electric displacement. Because the free-energy function is nonconvex, its derivative $\tilde{E}(\tilde{D})$ is not monotonic. Equation (37) has a graphic interpretation in Fig. 3(d): The nominal electric field \tilde{E}^* under which the two states coexist in equilibrium is at the level such that the two shaded regions have the same area. This interpretation is known as Maxwell's rule in the theory of phase transition. A similar interpretation holds for instability in structures, such as the propagation of bulges along a cylindrical party balloon and buckles along a pipe.^{46,47}

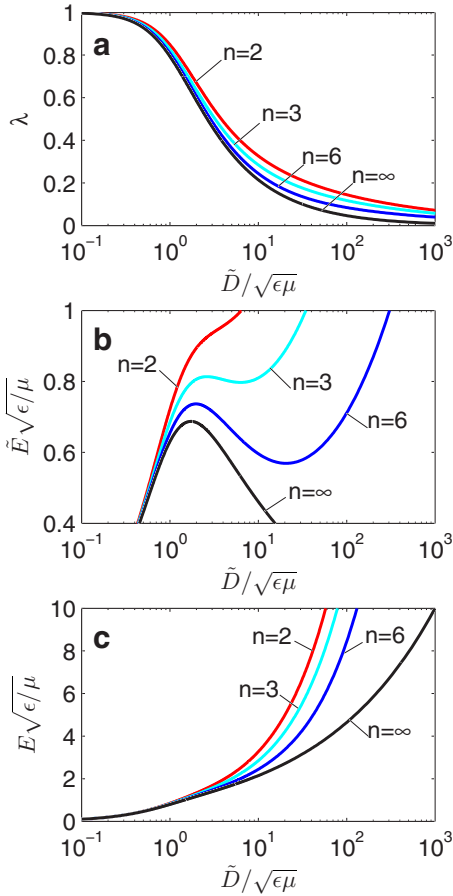


FIG. 4. (Color online) Electromechanical behavior of elastomers for several values of n , the number of links per chain. Various quantities are normalized by the small-strain shear modulus μ and the permittivity ε . (a) The function $\lambda(\tilde{D})$. (b) The function $\tilde{E}(\tilde{D})$ reaches a peak when $n=\infty$, is monotonic when $n < 2.6$, and reaches a peak and a valley when $2.6 < n < \infty$. (c) The true electric field is a monotonic function of the charge.

We expect that the experimental consequence of Fig. 3(d) also parallels that of a phase transition and structural instability. If the voltage is controlled, we expect that the elastomer exhibits a hysteresis loop, as indicated by the arrows in Fig. 3(d). In reality, the hysteresis loop may operate in an interval narrower than $(\tilde{E}_{valley}, \tilde{E}_{peak})$ because imperfections in elastomer may lower the barriers for switching from one state to the other in a small region, and then the area of the new state expands at the expense of the area of the old state. If the charge is controlled, we expect that the two states coexist at the voltage $L\tilde{E}^*$. As the charge ramps, the change of state occurs at a constant voltage.

We next apply our theory to the ideal dielectric elastomer. We specialize Eqs. (20) and (21) to

$$s = \frac{dW_s}{d\lambda} + \frac{\lambda\tilde{D}^2}{\varepsilon}, \quad \tilde{E} = \frac{\lambda^2\tilde{D}}{\varepsilon}. \quad (38)$$

When the elastomer is under no external force, $s=0$. When $n=\infty$, the degree of cross-link is low and $W_s(\lambda) = \mu(I-3)/2 = \mu(\lambda^2 + 2\lambda^{-1} - 3)/2$. Equation (38) reduces to

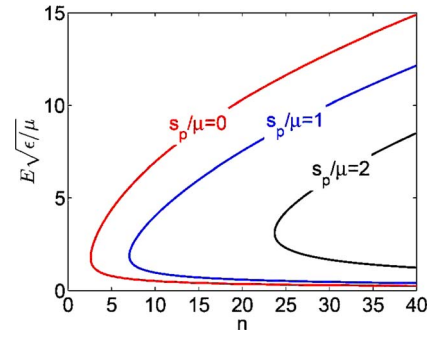


FIG. 5. (Color online) The coexistent states can be tuned by the degree of cross-link and the state of stress. A state of biaxial stress s_p is imposed in the plane of the elastomer layer. For given n and s_p/μ , the coexistent states have different true electric fields; they are intersections between a curve in the figure and a vertical line (not shown). Imposing an in-plane tension markedly reduces the true electric field in the thin state.

$$\lambda = \left(1 + \frac{\tilde{D}^2}{\mu\varepsilon}\right)^{-1/3}, \quad \frac{\tilde{E}}{\sqrt{\mu/\varepsilon}} = \frac{\tilde{D}}{\sqrt{\mu\varepsilon}} \left(1 + \frac{\tilde{D}^2}{\mu\varepsilon}\right)^{-2/3}. \quad (39)$$

The function $\lambda(\tilde{D})$ is monotonic [Fig. 4(a)], as expected. Figure 4(b) shows that the function $\tilde{E}(\tilde{D})$ has a peak: The left side of the curve in Fig. 4(b) corresponds to a convex part of the free energy, and the right side corresponds to a concave part of the free energy. The true electric field is $E = \tilde{E}/\lambda$, and the function $E(\tilde{D})$ is monotonic [Fig. 4(c)]. The peak nominal electric field is $\tilde{E}_{peak} \approx 0.69\sqrt{\mu/\varepsilon}$, which occurs when $\tilde{D} = \sqrt{3\varepsilon\mu}$, $\lambda \approx 0.63$, and $E \approx 1.1\sqrt{\mu/\varepsilon}$. The model suggests that if a region of the elastomer thins down to a critical thickness, the region should thin down further without limit.

The shape of the curve in Fig. 4(b) for the neo-Hookean material ($n=\infty$), however, is an exception rather than a rule. When n is finite, multiple terms in Eq. (27) are needed, leading to a much stiffer behavior as $\lambda \rightarrow 0$. Figure 4(b) plots the function $\tilde{E}(\tilde{D})$ for several values of n . Below a critical value, $n < 2.6$, the function $\tilde{E}(\tilde{D})$ is monotonic and the elastomer is electromechanically stable for the full range of electric field. When $2.6 < n < \infty$ (Fig. 4(b)), the function $\tilde{E}(\tilde{D})$ has the same shape as in Fig. 3(d). This shape is expected for most commonly used dielectric elastomers, given the large range of n .

Our theory can be extended to other loading conditions. As an illustration, let s_p be the nominal stress applied biaxially in the plane of the elastomer layer. In terms of the through thickness stretch λ , the in-plane stretch is $\lambda^{-1/2}$, so that the free energy becomes

$$G/LA = W(\lambda, \tilde{D}) - 2s_p\lambda^{-1/2} - \tilde{E}\tilde{D}. \quad (40)$$

For a fixed value of n and s_p , the two coexistent states are subject to the same voltage but have different true electric fields. In experiment, the true electric field in the thin state may exceed the electric breakdown strength. As shown in Fig. 5, imposing a biaxial stress significantly reduces the true electric field in the thin state and may enable the two states

to coexist. Furthermore, for a given n , the electromechanical instability can be averted when the biaxial stress is large enough. These conclusions are consistent with the experimental observations.¹⁰

V. CONCLUDING REMARKS

We have specified a material model that is consistent with the available experimental data and have shown that the free energy of commonly used dielectric elastomers is nonconvex, leading to coexistent states and hysteresis in elastomer layers. The theory also directs attention to several topics ripe for exploration. While we have explained the coexistence of flat and wrinkled states, we have not included wrinkles explicitly in our theory. When molecular groups in an elastomer can polarize nearly as freely as in liquids, e.g., when the degree of cross-link is low and the deformation is well below the fully extended limit, the dielectric behavior of the elastomer is expected to be liquidlike. It will be interesting to investigate how well the ideal dielectric elastomer represents a real one. The large flow of charge associated with the change of states may also lead to interesting applications. We hope that more refined experiment and theory will soon succeed in these explorations.

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APPENDIX: MAXWELL STRESS IN A VACUUM OR IN AN INCOMPRESSIBLE, LINEARLY DIELECTRIC FLUID

In his classic text, Maxwell derived an expression of stress in a vacuum due to an electrostatic field. His derivation is outlined here, which is referred to in several places in the body of the text. When a test charge q is placed in the vacuum, if we find that an external force must be applied on the charge to keep it stationary, we say that an electric field \mathbf{E} exists in the vacuum, such that

$$\mathbf{f} = q\mathbf{E}. \quad (\text{A1})$$

By convention, \mathbf{f} is called the electrostatic force, and the external force needed to maintain equilibrium is $-\mathbf{f}$. When a field of charge is present in the vacuum, denote the coordinate of a point in the vacuum by \mathbf{x} and the charge per unit volume by $q(\mathbf{x})$. Equation (A1) now represents a field of electrostatic force, with $-\mathbf{f}(\mathbf{x})$ being the external force per unit volume that must be applied to maintain the field of charge in equilibrium.

The field of charge $q(\mathbf{x})$ generates in the vacuum an electric field, which is governed by

$$\frac{\partial E_i}{\partial x_j} = \frac{\partial E_j}{\partial x_i}, \quad \frac{\partial E_i}{\partial x_i} = \frac{q}{\epsilon_0}, \quad (\text{A2})$$

where ϵ_0 is the permittivity of the vacuum.

Equations (A1) and (A2) together form a theory that can be tested experimentally. Given a field of charge $q(\mathbf{x})$, we can use Eq. (A2) to solve the electric field $\mathbf{E}(\mathbf{x})$ and then ascertain if we need to apply a field of external force $-\mathbf{f}(\mathbf{x})$, as predicted by Eq. (A1), to maintain the field of charge in equilibrium.

Inserting Eq. (A2) into Eq. (A1), one obtains

$$f_i = \frac{\partial}{\partial x_j} \left(\epsilon_0 E_i E_j - \frac{\epsilon_0}{2} E_k E_k \delta_{ij} \right). \quad (\text{A3})$$

This equation is reminiscent of the equilibrium equation in continuum mechanics. The quantity

$$\sigma_{ij} = \epsilon_0 E_i E_j - \frac{\epsilon_0}{2} E_k E_k \delta_{ij} \quad (\text{A4})$$

is known as the Maxwell stress.

The above is how Eq. (A4) was derived in Maxwell's text. The expression is also valid for an incompressible, linearly dielectric fluid, provided the permittivity of the vacuum, ϵ_0 , is replaced by that of the fluid, ϵ . The expression is not valid for a compressible fluid dielectrics or solid dielectrics. Maxwell said, "I have not been able to make the next step, namely, to account by mechanical considerations for these stresses in the dielectric. I therefore leave the theory at this point..."

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¹Y. Sugiyama and S. Hirai, *Int. J. Robot. Res.* **25**, 603 (2006).

²Q. M. Zhang, H. F. Li, M. Poh, F. Xia, Z. Y. Cheng, H. S. Xu, and C. Huang, *Nature (London)* **419**, 284 (2002).

³A. Sidorenko, T. Krupenkin, A. Taylor, P. Fratzl, and J. Aizenberg, *Science* **315**, 487 (2007).

⁴M. Warner and E. M. Terentjev, *Liquid Crystal Elastomers* (Clarendon, Oxford, 2003).

⁵R. Pelrine, R. Kornbluh, Q. B. Pei, and J. Joseph, *Science* **287**,

836 (2000).

⁶G. Kofod, W. Wirges, M. Paajanen, and S. Bauer, *Appl. Phys. Lett.* **90**, 081916 (2007).

⁷R. E. Pelrine, R. D. Kornbluh, and J. P. Joseph, *Sens. Actuators, A* **A64**, 77 (1998).

⁸F. Carpi and D. De Rossi, *IEEE Trans. Dielectr. Electr. Insul.* **12**, 835 (2005).

⁹G. Kofod, P. Sommer-Larsen, R. Kronbluh, and R. Pelrine, *J. Intell. Mater. Syst. Struct.* **14**, 787 (2003).

- ¹⁰J. S. Plante and S. Dubowsky, *Int. J. Solids Struct.* **43**, 7727 (2006).
- ¹¹E. M. Mockensturm and N. Goulbourne, *Int. J. Non-Linear Mech.* **41**, 388 (2006).
- ¹²S. M. Ha, W. Yuan, Q. B. Pei, R. Pelrine, and S. Stanford, *Adv. Mater. (Weinheim, Ger.)* **18**, 887 (2006).
- ¹³M. Wissler and E. Mazza, *Sens. Actuators, A* **A134**, 494 (2007).
- ¹⁴L. Patrick, K. Gabor, and M. Silvain, *Sens. Actuators, A* **A135**, 748 (2007).
- ¹⁵N. C. Goulbourne, E. M. Mockensturm, and M. I. Frecker, *Int. J. Solids Struct.* **44**, 2609 (2007).
- ¹⁶G. Gallone, F. Carpi, D. De Rossi, G. Levita, and A. Marchetti, *Mater. Sci. Eng., C* **27**, 110 (2007).
- ¹⁷J. S. Plante and S. Dubowsky, *Smart Mater. Struct.* **16**, S227 (2007).
- ¹⁸Y. Bar-Cohen, *J. Spacecr. Rockets* **39**, 822 (2002).
- ¹⁹Y. M. Liu, K. L. Ren, H. F. Hofmann, and Q. M. Zhang, *IEEE Trans. Ultrason. Ferroelectr. Freq. Control* **52**, 2411 (2005).
- ²⁰X. Q. Zhang, C. Lowe, M. Wissler, B. Jahne, and G. Kovacs, *Adv. Eng. Mater.* **7**, 361 (2005).
- ²¹A. Wingert, M. D. Lichter, and S. Dubowsky, *IEEE/ASME Trans. Mechatron.* **11**, 448 (2006).
- ²²R. Shankar, T. K. Ghosh, and R. J. Spontak, *Soft Matter* **3**, 1116 (2007).
- ²³G. Kofod, M. Paajanen, and S. Bauer, *Appl. Phys. A: Mater. Sci. Process.* **A85**, 141 (2006).
- ²⁴K. H. Stark and C. G. Garton, *Nature (London)* **176**, 1225 (1955).
- ²⁵L. A. Dissado and J. C. Fothergill, *Electrical Degradation and Breakdown in Polymers* (Peter Peregrinus, London, 1992).
- ²⁶M. Wissler and E. Mazza, *Sens. Actuators, A* **A120**, 184 (2005).
- ²⁷X. Zhao and Z. Suo, *Appl. Phys. Lett.* **91**, 061921 (2007).
- ²⁸K. H. Stark and C. G. Garton, *Nature (London)* **176**, 1225 (1955).
- ²⁹J. C. Maxwell, *A Treatise on Electricity and Magnetism* (Clarendon, Oxford 1998).
- ³⁰R. A. Toupin, *Journal of Rational Mechanics and Analysis* **5**, 849 (1956).
- ³¹A. C. Eringen, *Int. J. Eng. Sci.* **1**, 127 (1963).
- ³²H. F. Tiersten, *J. Acoust. Soc. Am.* **57**, 660 (1975).
- ³³G. Kofod and P. Sommer-Larsen, *Sens. Actuators, A* **A122**, 273 (2005).
- ³⁴M. Wissler and E. Mazza, *Smart Mater. Struct.* **14**, 1396 (2005).
- ³⁵R. P. Feynman, R. B. Leighton, and M. Sands, *The Feynman Lectures on Physics* (Addison-Wesley, Reading, MA, 1964).
- ³⁶Z. Suo, X. Zhao, and W. H. Greene, *J. Mech. Phys. Solids* (to be published).
- ³⁷R. M. McMeeking and C. M. Landis, *Trans. ASME, J. Appl. Mech.* **72**, 581 (2005).
- ³⁸A. Dorfmann and R. W. Ogden, *Acta Mech.* **174**, 167 (2005).
- ³⁹T. B. Xu, Z. Y. Cheng, and Q. M. Zhang, *Appl. Phys. Lett.* **80**, 1082 (2002).
- ⁴⁰S. F. Liu, S. E. Park, L. E. Cross, and T. R. ShROUT, *J. Appl. Phys.* **92**, 461 (2002).
- ⁴¹J. Su, T. B. Xu, S. J. Zhang, T. R. ShROUT, and Q. M. Zhang, *Appl. Phys. Lett.* **85**, 1045 (2004).
- ⁴²T. B. Xu and J. Su, *J. Appl. Phys.* **97**, 034908 (2005).
- ⁴³L. R. G. Treloar, *The Physics of Rubber Elasticity* (Clarendon, Oxford, 1975).
- ⁴⁴M. C. Boyce and E. M. Arruda, *Rubber Chem. Technol.* **73**, 504 (2000).
- ⁴⁵E. M. Arruda and M. C. Boyce, *J. Mech. Phys. Solids* **41**, 389 (1993).
- ⁴⁶E. Chater and J. W. Hutchinson, *J. Appl. Mech.* **51**, 269 (1984).
- ⁴⁷E. Corona and S. Kyriakides, *Int. J. Solids Struct.* **24**, 505 (1988).