Electrostriction of Polar Glasses

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Abstract

We develop a finite temperature theory for the susceptibility and electrostriction of isotropic substances in which permanent electric dipoles are restrained from free rotation by elastic forces. All parameters are constrained by the measured susceptibility and elastic constants. When applied to polyurethane, the predicted electrostriction is approximately consistent with some of the wide range of data. The saturation of the electrostriction at high field may be explained qualitatively if the dipoles consist of several amide groups locked together by crystallization of the hard segments of the polymer.

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I. INTRODUCTION

Zhenyi, et al. [1] discovered that the electrostriction of polyurethane film is large enough to be interesting. The measurements of Wang, et al. [2] found a smaller electrostriction. The experiments are unexpectedly difficult, partly because the material is hygroscopic and its properties history-dependent, and partly because the measured electrostriction is affected by the confinement of the soft polyurethane by any stiffer material (such as electrodes) with which it is in contact.

Comparatively little work exists [3,4] on the theory of electrostriction, and none directly applicable to this problem. We develop a simple theory of the electric susceptibility of polymers (such as polyurethane) with polar groups, and calculate electrostriction from the susceptibility. The theory has one parameter, which may be determined by comparing to the observed susceptibility.

II. SUSCEPTIBILITY

Polyurethane elastomers are block copolymers containing crystallizable and noncrystallizable segments [1]. The molecular structure of a generic polyurethane is shown in Figure 1, with $x$ typically about 2. The crystallizable (hard) segments have attached amide groups with permanent electric dipole moments $p \approx 3.6 \times 10^{-18}$ esu-cm. Our model for the susceptibility considers the orientation of the dipoles in the electric field, and for the moment neglects the intrinsic susceptibility of the nonpolar portions of the polyurethane. For comparison, nonpolar polymers such as polyethylene typically have dielectric constants (resulting entirely from polarization of the chemical bonds) of about 2.3, while polyurethanes have dielectric constants of about 6.8.

We make an independent particle approximation in which the dipoles in electrified polyurethane have two contributions to their energy—the usual electrostatic energy

$$U_1 = -p \cdot E,$$  \hspace{1cm} (2.1)
and a term resulting from their rotation from their equilibrium orientations. This latter energy results from the elastic restoring forces of the polymer chains and of the bulk medium (entangled chains). For small deviations $\Delta \theta \ll 1$ from the equilibrium position the elastic energy will, in general, be quadratic in $\Delta \theta$. We therefore write

$$U_2 = \frac{1}{2} S (\Delta \theta)^2,$$  \hspace{1cm} (2.2)

where $S$ is an elastic stiffness constant. For simplicity we assume that $S$ is a scalar so that $U_2$ depends only on the magnitude of the angular deflection, and not on its direction; this may not be true for dipoles on a polymer, but in the absence of a detailed model for the orientation of the amide groups in polyurethane it is a reasonable approximation. If the applied electric field defines the $\theta = 0$ axis of a polar coordinate system, and the orientation of the dipole defines the $\phi = 0$ plane and makes an angle $\theta$ to the electric field, then $\Delta \theta$ is obtained from

$$\cos \Delta \theta = \sin \theta_0 \sin \theta \cos \phi_0 + \cos \theta_0 \cos \theta,$$  \hspace{1cm} (2.3)

where $(\theta_0, \phi_0)$ is the equilibrium position of the dipole in the absence of a field.

Unfortunately $2.2$ becomes cumbersome when $2.3$ is substituted, and the integrals required to take thermal averages cannot be done analytically. Therefore, we replace $2.2$ by

$$U_2 = S (1 - \cos \Delta \theta).$$  \hspace{1cm} (2.4)

To second order in $\Delta \theta$ $2.4$ agrees with $2.2$. Because the actual calculation of $U_2$ for large $\Delta \theta$ is a problem in nonlinear elasticity, which would be quite difficult, there is no reason to think that $2.4$ is any less accurate than $2.2$. The form $2.4$ may be rewritten

$$U_2 = S - \mathbf{p} \cdot \mathbf{\tilde{E}},$$  \hspace{1cm} (2.5)

where $\mathbf{\tilde{E}}$ is a vector with the dimensions of an electric field which points in the direction of the equilibrium position of the dipole (for $\mathbf{E} = 0$), and which has magnitude $\mathbf{\tilde{E}} = S/p$. The
effects of the elastic forces on the dipole have now been incorporated into the field $\tilde{E}$, which will be assumed to be an isotropic random function of space with zero correlation length and fixed modulus $\tilde{E}$. The total energy $U = U_1 + U_2$ may be obtained from (2.1) and (2.5), dropping the constant term in (2.3):

$$U = -\mathbf{p} \cdot (\mathbf{E} + \tilde{\mathbf{E}}).$$  \hspace{1cm} (2.6)

We ignore the electrostatic and elastic interaction between dipoles, in effect assuming their density to be low. The physics of randomly oriented dipoles embedded in an amorphous elastic polymer matrix is described by the random field $\tilde{E}$. If interactions between dipoles were to be included the problem would be that of a dipole glass, analogous to the familiar (but difficult) spin glass problem.

We evaluate the mean polarization $\langle \mathbf{p} \rangle$ in thermal equilibrium at temperature $T$. For a given dipole the energy (2.6) leads, by the usual elementary calculation, to a polarization of magnitude

$$|\langle \mathbf{p} \rangle_T| = L(x_c) p$$  \hspace{1cm} (2.7)

along the direction of $\mathbf{E} + \tilde{\mathbf{E}}$, where the Langevin function

$$L(x) \equiv \coth(x) - \frac{1}{x},$$  \hspace{1cm} (2.8)

the combined normalized effective field strength is

$$x_c \equiv \frac{|\mathbf{E} + \tilde{\mathbf{E}}|}{kT},$$  \hspace{1cm} (2.9)

and $\langle \rangle_T$ denotes a thermal average only.

The net polarization of the medium must, by symmetry, be in the direction ($\hat{z}$) of the applied field $\mathbf{E}$, and is found from

$$\frac{\langle p_z \rangle_T}{p} = \frac{1}{4\pi} \int L(x_c) \cos \theta' d\Omega,$$  \hspace{1cm} (2.10)

where the overline represents a quenched angular average over all directions of $\mathbf{E}$ and $\theta'$ is the angle between $\mathbf{E}$ and $\mathbf{E} + \tilde{\mathbf{E}}$. Upon expanding $L(x_c)$ and $\cos \theta'$ in powers of $\delta \equiv E/\tilde{E}$
and \( \xi \equiv pE/kT = x_0 \delta \), where \( x_0 \equiv p\tilde{E}/kT \), and keeping only terms of first order in \( E \), we find

\[
\frac{\langle p_z \rangle_T}{p} = \frac{2}{3} \delta L(x_0) + \frac{1}{3} \xi L'(x_0).
\] (2.11)

Note that while \( \delta \ll 1 \) and \( \xi \ll 1 \) are assumed, \( x_0 \) is generally not small. For a density \( n \) of independent dipoles the macroscopic polarization \( P = n\langle p \rangle_T \) may be obtained from (2.11):

\[
P = np\frac{E}{E} \left[ \frac{2}{3} L(x_0) + \frac{1}{3} x_0 L'(x_0) \right] = np\frac{E}{E} f(x_0).
\] (2.12)

The function \( f(x) \) is plotted in Figure 2. The limits of (2.12) are

\[
P \approx \begin{cases} 
\frac{np^2E}{3kT}, & \text{if } x_0 \ll 1; \\
\frac{2npE}{3E}, & \text{if } x_0 \gg 1.
\end{cases}
\] (2.13)

The limit for \( x_0 \ll 1 \) is a familiar elementary result, while the limit for \( x_0 \gg 1 \) was given in slightly different form by Frölich [5].

Polyurethanes typically have dielectric constants \( \epsilon \approx 6.8 \). Using the relation (in cgs units) \( \epsilon = 1 + 4\pi \chi \), this yields a susceptibility \( \chi = 0.46 \). The self-consistent molecular polarizability \( \gamma \) (here a scalar, but in general a tensor) is

\[
\frac{p}{E} f \left( \frac{p\tilde{E}}{kT} \right) = \frac{\langle p_z \rangle_T}{E} \equiv \gamma = \frac{3}{4\pi n} \left( \frac{\epsilon - 1}{\epsilon + 2} \right),
\] (2.14)

where the last equality is the Clausius-Mossotti equation [3]. This equation may be modified straightforwardly to allow for a dielectric constant \( \epsilon_c \) of the continuum in which the dipoles are embedded. The result is

\[
\frac{p}{E} f \left( \frac{p\tilde{E}}{kT} \right) = \gamma = \frac{3}{4\pi n} \left( \frac{\epsilon - \epsilon_c}{\epsilon + 2} \right).
\] (2.15)

For the polyurethane shown in Figure [4] with \( x = 2 \) and density 1.1 gm/cm\(^3\), the dipole density \( n = 3.4 \times 10^{21} \) cm\(^{-3}\), assuming each amide group rotates independently. Then, with \( p = 3.6 \times 10^{-18} \) esu-cm, the self-consistent solution to the transcendental equation (2.13), taking \( T = 300^\circ \)K and \( \epsilon_c = 2.3 \), is \( p\tilde{E}/kT = 5.2 \), i.e. \( \tilde{E} = 6.1 \times 10^4 \) cgs (= 1.8 \( \times 10^7 \) V/cm).
It should be remembered that these numerical values depend on the assumed numerical values of $n$ and $p$, which are poorly known.

The twisting stiffness constant equivalent to the derived value of $\tilde{E}$ is $S = \tilde{E}p = 2.2 \times 10^{-13}$ erg. This may be compared to the macroscopic elastic constants of polyurethane, which typically has a Young’s modulus $Y \approx 3 \times 10^8$ dyne/cm$^2$. If the dipole is described by a rigid sphere of radius $a$, then rotation by an angle $\Delta \theta$ implies a strain $\sim \Delta \theta$, a tangential stress on the surface of the sphere $\sim Y \Delta \theta$, and a total torque $\sim 2\pi Ya^3 \Delta \theta$. The corresponding stiffness constant $S \approx 2\pi Ya^3$, so that $a \approx 5\text{Å}$. This value is not unreasonable, although perhaps a bit large, but its significance is uncertain: The dipoles are mechanically coupled to their environment in complex ways. They are parts of a nearly inextensible and flexurally stiff covalently bonded polymer chain, which can shear quite easily with respect to its neighbors, except as limited by entanglements. These elastic properties are strongly temperature dependent, so that $\tilde{E}$ will also be sensitive to temperature, at least for temperatures of order room temperature. Most of the temperature dependence of 2.11 and 2.12 is likely to come from the variation of $\tilde{E}$ with $T$, rather than from the explicit dependence on $T$, except perhaps at very low temperatures. In fact, some polar polymers are known [7] to have values of $\epsilon$ which increase rapidly with $T$, as this argument would suggest.

### III. SATURATION

The derivation of 2.12 is limited to small electric fields. The effective electric field $E_{eff}$ acting on an object in an amorphous medium is (in cgs units)

$$E_{eff} = E + \frac{4\pi}{3} P = E \left(\frac{\epsilon + 2}{3}\right) \approx 2.9E, \quad (3.1)$$

where we have taken the empirical dielectric constant of polyurethane. In order for 2.12 to be valid the conditions $pE_{eff} \ll kT$ and $E_{eff} \ll \tilde{E}$ must both be met; when they are not met $\langle p_z \rangle$ becomes a significant fraction of $p$, the polarization saturates, and $\epsilon$, $\chi$, and the
electrostriction decrease below the values given by the low field theory. The available strong-field data [1] only describe the electrostriction, and show that it saturates at $E \approx 10^7 \text{V/m} \approx 300 \text{ cgs}$, corresponding to $E_{\text{eff}} \approx 900 \text{ cgs}$, $pE_{\text{eff}}/kT \approx 0.1$, and $E_{\text{eff}}/\bar{E} \approx 0.02$. We expect the susceptibility to saturate at the same field strengths as does the electrostriction, a prediction which is readily tested.

The electrostriction saturates at fields substantially smaller than expected. This discrepancy may be resolved if the actual rotating dipole moments consist of a number of individual amide groups, locked together by crystallization of the hard segments of the polymer. Such a rigid block would have a value of $p$ several times that of an individual amide group, and $n$ would represent the density of such blocks and would be correspondingly smaller than the density of individual amide groups. The value of $np$ would not be greatly changed by this locking of individual amides into a single giant dipole. Because $f(x)$ is a slowly varying function for $x \gg 1$, $\bar{E}$ would also not be greatly changed.

IV. ELECTROSTRICTION

The Landau theory of electrostriction defines a free energy per unit volume of a body in an imposed stress field $\sigma_{ij}$ and electric field $E_i$:

$$F(\sigma_{ij}, E_i) = \mu u_{ij}^2 + \frac{1}{2} \lambda u_{mm}^2 - u_{ij} \sigma_{ij} + \frac{1}{2} (\chi^{-1})_{ij} P_i P_j + Q_{ijkl} P_i P_j u_{kl} - E_i P_i,$$  \hspace{1cm} (4.1)

where $\mu$ and $\lambda$ are Lamé coefficients of elasticity, $u_{ij}$ is the strain tensor, $\sigma_{ij}$ is the stress tensor, $(\chi^{-1})_{ij}$ is the inverse of the susceptibility tensor $\chi_{ij}$ defined by $P_i = \chi_{ij} E_j$, $Q_{ijkl}$ is the electrostriction tensor, and $P_i$ and $E_i$ are the polarization and electric field. In this theory $u_{ij}$ and $P_i$ describe the internal state of the material, and characterize its response to the externally imposed parameters $\sigma_{ij}$ and $E_i$. If we neglect fluctuations, which are small far from phase transitions, $u_{ij}$ and $P_i$ may be found by minimizing [4.1].

By multiply differentiating the Legendre transform of [1.1]

$$G(\sigma_{ij}, E_i) \equiv F + u_{ij} \sigma_{ij} + E_i P_i,$$  \hspace{1cm} (4.2)
in various orders we can relate $Q_{ijkl}$ to the derivatives of $(\chi^{-1})_{ij}$ with respect to $u_{kl}$:

$$Q_{ijkl} = \frac{\partial}{\partial P_i} \frac{\partial}{\partial P_j} \frac{\partial G}{\partial u_{kl}} = \frac{\partial}{\partial u_{kl}} \frac{\partial G}{\partial P_i} \frac{\partial}{\partial P_j},$$  \hspace{1cm} (4.3)

i.e.,

$$Q_{ijkl} = \frac{\partial}{\partial P_i} \frac{\partial}{\partial P_j} \sigma_{kl} = \frac{\partial}{\partial u_{kl}} (\chi^{-1})_{ij},$$  \hspace{1cm} (4.4)

where (4.4) has been obtained by using the thermodynamic relations $\partial G/\partial u_{kl} = \sigma_{kl}$ and $(\chi^{-1})_{ij} = \partial^2 G/\partial P_i \partial P_j$. We then use our elementary microscopic model of $\chi$ to calculate $Q_{ijkl}$ from the second part of (4.4): $Q_{ijkl} = \partial (\chi^{-1})_{ij}/\partial u_{kl}$.

The application of a strain component $u_{33}$ to an isotropic distribution of vectors $\vec{E}$ (the equilibrium orientations of the dipoles) rotates them. We assume that the magnitude $\vec{E}$ is not changed by the application of the strain field. We do not know if this is true, but it could not be described except by a completely phenomenological parameter, which we have no independent means of determining. The angle between $\vec{E}$ and the $\theta = 0$ axis is rotated by an amount, found from elementary geometry

$$\Delta \theta = -u_{33} \sin \theta \cos \theta.$$  \hspace{1cm} (4.5)

The calculation of susceptibility is then repeated, replacing $\theta$ by $\theta + \Delta \theta$, with the result, correct to first order in $u_{33}$,

$$\gamma_{33} \equiv \frac{\langle p_z \rangle_T}{E_z} = \frac{p}{E} \left[ f(x_0) + g(x_0) u_{33} \right],$$  \hspace{1cm} (4.6)

where the function $g(x)$ is defined

$$g(x) \equiv -\frac{4}{15} \left[ L(x) - xL'(x) \right],$$  \hspace{1cm} (4.7)

and is plotted in Figure 2. By considerations of symmetry (or explicit calculation) it is seen that $\gamma_{ij} = \overline{\langle p_i \rangle_T / \partial E_j}$ is diagonal, as is $\chi_{ij}$, so that $(\chi^{-1})_{33} = (\chi_{33})^{-1}$. Then, to lowest order in $u_{33}$, noting that $\Delta n = -u_{33} n$ and $\partial (\chi^{-1})_{ij} / \partial (n \gamma^{-1})_{ij} = 1$, we have

$$Q_{3333} = \frac{\partial (\chi^{-1})_{33}}{\partial u_{33}} \approx \frac{\vec{E}}{npf(x_0)} \left( 1 - \frac{g(x_0)}{f(x_0)} \right).$$  \hspace{1cm} (4.8)
We have neglected the dependence on strain of the susceptibility of the continuum medium in which the dipoles are embedded; any such dependence is likely to be very small, especially in a soft elastomer in which deformations are almost purely volume-conserving.

The effects of strain components \( u_{11} \) and \( u_{22} \) may be found similarly:

\[
\Delta \theta = (u_{11} \sin^2 \phi + u_{22} \cos^2 \phi) \sin \theta \cos \theta,
\]

where \( \phi \) is the azimuthal angle of \( \mathbf{E} \), measured from the y-axis. Then

\[
Q_{3311} = Q_{3322} = \frac{\mathbf{E}_{npf}(x_0)}{npf(x_0)} \left( 1 + \frac{g(x_0)}{2f(x_0)} \right).
\]

Similar calculations for \( u_{12}, u_{13}, \) and \( u_{23} \) (or symmetry arguments) show that

\[
Q_{33kl} = 0 \quad \text{for } k \neq l.
\]

Similarly, because the distribution of \( \mathbf{E} \) retains inversion symmetry in the strained state in all of these strained configurations \( \chi_{ij} \) remains diagonal, so that \( Q_{ijkl} = 0 \) for \( i \neq j \).

Permutation of indices leads to the general result

\[
Q_{ijkl} = \begin{cases} 
\frac{\mathbf{E}_{npf}(x_0)}{npf(x_0)} \left( 1 - \frac{g(x_0)}{f(x_0)} \right) & \text{for } i = j = k = l; \\
\frac{\mathbf{E}_{npf}(x_0)}{npf(x_0)} \left( 1 + \frac{g(x_0)}{2f(x_0)} \right) & \text{for } i = j \neq k = l; \\
0 & \text{otherwise.}
\end{cases}
\]

We now calculate the electrostrictive strain produced by the application of an electric field and polarization in the \( z \) direction. Differentiating \( 4.1 \) with respect to \( u_{kl} \), and setting the derivative equal to zero in equilibrium yields

\[
0 = 2\mu u_{kl} + \sigma_{kl} + Q_{ijkl}P_iP_j.
\]

The electrostrictive term acts as an effective stress

\[
\sigma'_{kl} = -Q_{ijkl}P_iP_j.
\]

Note that linearizing \( 4.13 \) about a state of nonzero \( \mathbf{E} = (E_0 + \Delta E)\hat{z} \) leads to
\[ \Delta \sigma'_{kl} = -2Q_{33kl} \frac{\partial P(E_0)}{\partial E} P(E_0) \Delta E; \]  

(4.16)

i.e., an effective piezoelectric response. Using (4.8), (4.10) and (4.11) yields

\[ \sigma'_{11} = \sigma'_{22} = -\frac{\tilde{E}}{npf(x_0)} \left( 1 + \frac{g(x_0)}{2f(x_0)} \right) P^2_3 \]  

(4.17)

\[ \sigma'_{33} = -\frac{\tilde{E}}{npf(x_0)} \left( 1 - \frac{g(x_0)}{f(x_0)} \right) P^2_3; \]  

(4.18)

the off-diagonal components are zero. Substitution in the elastic stress-strain relation (or use of (4.13)) yields the strain

\[ u_{11} = u_{22} = \left( -\frac{\tilde{E}}{4\mu np} \frac{g(x_0)}{f^2(x_0)} + \frac{\tilde{E}}{3Kn np} \frac{1}{f(x_0)} \right) \chi E^2_3 \]  

(4.19)

\[ u_{33} = \left( \frac{\tilde{E}}{2\mu np} \frac{g(x_0)}{f^2(x_0)} + \frac{\tilde{E}}{3Kn np} \frac{1}{f(x_0)} \right) \chi E^2_3, \]  

(4.20)

where the bulk modulus \( K = \lambda + \frac{2}{3} \mu \).

In order to rewrite (4.20) in terms of \( E_3 \) the Clausius-Mossotti equation (2.14, 2.15) may be solved for \( \chi \) in terms of \( f(x_0) \), but because \( \chi \) is measured it is easier simply to substitute \( P = \chi E \):

\[ u_{11} = u_{22} = \left( -\frac{\tilde{E}}{4\mu np} \frac{g(x_0)}{f^2(x_0)} + \frac{\tilde{E}}{3Kn np} \frac{1}{f(x_0)} \right) \chi E^2_3 \]  

(4.21)

\[ u_{33} = \left( \frac{\tilde{E}}{2\mu np} \frac{g(x_0)}{f^2(x_0)} + \frac{\tilde{E}}{3Kn np} \frac{1}{f(x_0)} \right) \chi E^2_3. \]  

(4.22)

For materials which are soft to shear, with \( \mu \ll K \) (as in many polymers) the second terms in parentheses of (4.20) and (4.22) are small compared to the first terms. It is evident that materials with small shear moduli \( \mu \) (or small Young’s moduli, equal to \( 3\mu \) in the limit \( \mu/K \to 0 \)) will show comparatively large electrostrictive strains. In addition, even though typically \( Q \propto \chi^{-1} \), the strain \( u \propto \chi \) and materials with large \( \chi \) (but small \( Q \)) are usually the best electrostrictors [8].
V. COMPARISON TO EXPERIMENTS

Substitution in (4.22) for PT6100S polyurethane [1], which has \( \mu \approx 3 \times 10^7 \text{ erg/cm}^3 \), taking \( K \gg \mu \), and using the estimated \( n \) and \( p \) and the value of \( \tilde{E} \) previously determined from the susceptibility, yields \( u_{33} = -7 \times 10^{-9} \text{ cm}^4/\text{esu}^2 E_3^2 \), where the esu is the cgs unit of charge \((1/(3 \times 10^9) \text{ Coulomb})\). Zhenyi, et al. [1] find \( u_{33} \approx -2 \times 10^{-8} \text{ cm}^4/\text{esu}^2 E_3^2 \), but with a range of values of a factor \( \sim 2 \) depending on the details of sample preparation and of mechanical constraint during the experiments.

Wang et al. [2] find for 80CF-2 polyurethane \( u_{33} \approx -3 \times 10^{-9} \text{ cm}^4/\text{esu}^2 E_3^2 \) (approximately 40% of the effect results from Maxwell stress rather than electrostriction). For this material \( \mu \approx 1.0 \times 10^8 \text{ erg/cm}^3 \) [2] so that we predict (4.22) \( u_{33} \approx -2.4 \times 10^{-9} \text{ cm}^4/\text{esu}^2 E_3^2 \), approximately consistent with experiment. The result (4.22) contains no free parameters because the ratio \( \tilde{E}/(np) \) is determined from the measured dielectric constant by (2.13), as is \( \chi \), and \( \mu \) is directly measured.

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APPENDIX A: VOLUME TORQUES

It is evident that there are no body forces on a uniformly electrified homogeneous material, but it is still of interest to examine the strain field \( u \) produced by a point torque in an elastic medium, such as the permanent dipoles in electric fields discussed in this paper, in order to see if this strain contributes to the electrostriction. This result not readily found in the elasticity literature.
Begin with Kelvin’s result for the displacement field $u$ produced by a point force $F$ at the origin of an elastic medium $[9]$:

$$u(r) = \left(\frac{1 + \sigma}{8\pi Y(1 - \sigma)}\right) \left((3 - 4\sigma)F + \hat{n}(\hat{n} \cdot F)\right) \frac{r}{r^3},$$

(A1)

where $\sigma$ is Poisson’s ratio, $r$ denotes the point at which the displacement is measured, and $\hat{n}$ is the unit vector in the direction of $r$. By adding to (A1) the displacement produced by a force $-F$ acting at a point $\Delta r$ we find the displacement produced by a point torque $N = -\Delta r \times F$:

$$u(r) = \left(\frac{1 + \sigma}{8\pi Y(1 - \sigma)}\right) \frac{N \times r}{r^3}.$$

(A2)

A dipole $p$ in an electric field $E$ is subject to a torque

$$N = p \times E.$$

(A3)

In a medium with an inversion-symmetric distribution of dipole orientations $\langle p \rangle = 0$ and $\langle N \rangle = 0$. Each dipole is rotated by an angle $\Delta \theta = N/S$.

The rotation of the dipoles changes the direction of their moments, and therefore the torque. The change in $p$ is

$$\Delta p = \Delta \theta \times p = \frac{N \times p}{S} = \frac{(p \times E) \times p}{S} = \frac{E p^2 - p(p \cdot E)}{S},$$

(A4)

and yields an incremental torque, second order in $E$ (like the electrostriction):

$$N = \Delta p \times E = -\frac{(p \times E)(p \cdot E)}{S}.$$

(A5)

Although (A5) is second order in both $p$ and $E$, in any volume element it will average to zero for an inversion-symmetric distribution of $p$, and hence it is not a useful model of electrostriction.

APPENDIX B: CORRELATION OF ELECTROSTRICTION WITH THERMAL EXPANSION

Uchino, et al. [10] note that the electrostriction coefficient $Q$ and the thermal expansion coefficient $\alpha$ are empirically related by $Q \propto \alpha^2$ for a wide variety of materials, including one
polymer (PVDF), pyrex glass, ceramic piezoelectrics, and ionic crystals (see their Figure 1); there is only a factor of 2 (in $\alpha$) or 4 (in $Q$) scatter about the power law fit, which extends over a range of about 30 in $\alpha$ (1000 in $Q$). This empirical relation has a very elementary explanation.

The simplest model of thermal expansion is a particle in a weakly anharmonic potential $V = ax^2 + bx^3$. If the particle has an energy $kT$, its turning points are shifted by $\Delta x \approx -bkT/(2a^2)$, giving a linear thermal expansion coefficient $\alpha = |b|/(2a^2a_0)$, where $a_0$ is the distance between the potential minimum and the origin (or the nearest neighboring particle).

The analogous simple model of electrostriction considers two particles in the well, with charges $\pm q$, and adds an electric field $E$. The particles are now in potentials $V_{\pm} = ax_{\pm}^2 + bx_{\pm}^3 \pm qE x_{\pm}$, and their equilibrium ($T = 0$) positions are given by $x_{\pm} = -a + \sqrt{a^2 \pm 3bqE}/(3b)$. The displacement of their barycenter is $\Delta x = (x_+ + x_-)/2 \approx -3bq^2E^2/(8a^4)$, giving an electrostrictive coefficient $Q = -3bq^2/(8a^4a_0)$ (note that $b < 0$ for realistic potentials).

If the chief variation between materials is in $a$ then $Q \propto \alpha^2$, as observed; the scatter about this relation arises from variations in $b$, $a_0$, and the effective charge $q$. The parameter $a$ is related to the bulk modulus, which varies a great deal between materials; it is not surprising that variations in the other variables are less important, though not insignificant.

**APPENDIX C: ELECTROSTRICTION IN THE MELT**

It is possible to construct a very simple model of electrostriction of a melted polyurethane, with no elastic resistance to rotation of the permanent dipoles. Suppose the polymer configuration to be a random walk which deviates from isotropy because an applied electric field distorts the equilibrium distribution of the orientations of the dipoles (for small anisotropy the self-avoiding property of the walk will not change the degree of anisotropy). Consider dipole components $p_{\perp}$ perpendicular to a fraction $f$ of the units of the polymer chain, but otherwise free to rotate. The distribution of dipole orientations making an angle $\theta$ with respect to an electric field in the $z$ direction is given by the elementary result
\[ P(\theta) = \frac{ve^{-v\cos \theta}}{2 \sinh v}, \]  

where \( v \equiv p_\perp E_{\text{eff}}/kT \) and \( E_{\text{eff}} = (1 + \frac{4\pi}{3}\chi)E \) is the effective field at a dipole in a random medium. Each polymer \( \mathbf{r}(s) \) can now be regarded as a biased random walk, whose mean square end-to-end distance grows anisotropically as a function of arc length \( \langle [r_i(s) - r_i(0)] [r_j(s) - r_j(0)] \rangle = (2D_{ij}s)^{2\eta} \). For chain elements of unit length the random walk is described by a diagonal diffusion tensor, correct to second order in \( u \),

\begin{align*}
D_{xx} &= \frac{1}{2} \left( \langle y_d^2 \rangle + \langle z_d^2 \rangle \right) = \frac{1}{3} \left( 1 + \frac{fu^2}{30} \right) \\
D_{yy} &= \frac{1}{2} \left( \langle x_d^2 \rangle + \langle z_d^2 \rangle \right) = \frac{1}{3} \left( 1 + \frac{fu^2}{30} \right) \\
D_{zz} &= \frac{1}{2} \left( \langle x_d^2 \rangle + \langle y_d^2 \rangle \right) = \frac{1}{3} \left( 1 - \frac{fu^2}{15} \right),
\end{align*}

where the subscript \( d \) refers to the components of the dipole vectors. The corresponding strain is

\[ u_{zz} = -\frac{f\eta}{15} \left( \frac{p_\perp}{kT} \right)^2 \left( 1 + \frac{4\pi}{3}\chi \right)^2 E^2 = -2.7 \times 10^{-9} E^2 \]

\[ u_{xx} = u_{yy} = -\frac{u_{zz}}{2}, \]

where we have taken \( f = 0.2, \eta = 0.6, p_\perp = 2.5 \times 10^{-18} \text{ esu-cm}, T = 300^\circ K, \) and \( \chi = 0.46 \) (corresponding to solid polyurethane with \( \epsilon = 6.8 \)). This strain will make the material optically active, but in order to calculate this it would be necessary to know the intrinsic dielectric anisotropy of the polymer chain at optical frequencies; optical activity is determined by the strain alone, and is not specific to its electrostrictive origin.
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FIGURES

FIG. 1. Molecular structure of polyurethane elastomer.

FIG. 2. The functions $f(x)$ and $g(x)$
