Anomalous Elasticity of Piezoelectric Nanotubes

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I. MODEL EQUATIONS

We will discuss a general case that can be applied to any piezoelectric nanotube or wire shaped piezoelectrics. When an external force (eg. stretch) is applied to the end of the tube, the elastic strain is coupled to the electric polarization through the piezoelectric coefficients. Unlike the 3D bulk material in which a uniform polarization will be present and charge can only distribute at the interface, a spatial variation of the polarization takes place in 1D piezoelectric systems. The bound charges thus also is spatially varying along the tube. Similarly one can also consider an alternative case where an uniform electric field is applied across the tubes and result spatial varying mechanical stresses. In the current study, we consider the former case where the applied field is the stress.

We begin by considering a piezoelectric tube with parameters: L = length, R = radius, C=1D elastic modulus, e = 1D piezoelectric constant. The spatially varying bound charge density is then defined as a function of position $\rho(z)$. The free energy can be expressed as the sum of the elastic energy, the electrostatic energy between the bound charges and the external stress energy

$$\begin{aligned} G &= \frac{1}{2}\sum_{\alpha=\beta} C_{\alpha\beta}\int_0^\infty \eta_\alpha(z)\eta_\beta(z)dz \\ &\quad + \frac{1}{2}\sum_{\alpha,\beta} e_\alpha e_\beta \int_0^\infty\int_0^\infty \frac{\partial\eta_\alpha(z)}{\partial z}V(z-z')\frac{\partial\eta_\beta(z')}{\partial z'}dzdz' \\ &\quad - \sum_\alpha \int \eta_\alpha(z) f_\alpha(z)dz \end{aligned} \tag{1}$$

where $V(z-z')$ is the Coulomb kernel between two charges rested on two rings along the tube separated by $z-z'$. The Euler-Lagrange equation $\frac{\partial G}{\partial\eta(z)} = 0$ minimizing G must be satisfied at all points on the tube, ie.

$$\eta(z) = \frac{B}{C}\int_0^L \frac{\partial V(z-z')}{\partial z}\frac{\partial\eta(z')}{\partial z'}dz' - \frac{f(z)}{C} \tag{2}$$

This equation sets the equilibrium condition under the elastic, external and electrostatic force in order to stabilize the tube geometry.

A. Analytic solution

To solve for Eq. 2, we write the Coulomb force into a Fourier transform

$$\begin{aligned} &\int_0^L \frac{\partial V(z-z')}{\partial z}\frac{\partial\eta(z')}{\partial z'}dz' \\ &= \int_0^L\int_0^\infty iqV(q)e^{iq(z-z')}dq\int_0^\infty iq'\eta(q')e^{iq'z'}dq'dz' \\ &= \int_0^L dq\int_0^\infty dq' iqiq'V(q)\eta(q')e^{iqz}\int_0^L e^{i(q'-q)z'}dz' \\ &= -\int_0^\infty dq\int_0^\infty dq' qq'V(q)\eta(q')e^{iqz}\delta(q-q') \\ &= -\int_0^\infty dq q^2 V(q)\eta(q)e^{iqz} \end{aligned} \tag{3}$$

Note that if we let $g_1(z-z') = \frac{\partial V(z-z')}{\partial z}$ and $g_2(z) = \frac{\partial\eta(z)}{\partial z}$, then we get $g_1(q) = iqV(q)$ and $g_2(q) = iq\eta(q)$. Therefore in the momentum space, Eq. 2 becomes

$$\eta(q) = -\frac{B}{C}q^2V(q)\eta(q) - \frac{f(q)}{C} \tag{4}$$

Solve for $\eta(q)$ we get

$$\eta(q) = -\frac{\frac{f(q)}{C}}{\frac{B}{C}q^2V(q)+1} \tag{5}$$

Let's assume the applied force is a step function $f(z) = fH(z)$, then

$$f(q) = \pi\delta(q) - \frac{i}{q} \tag{6}$$

Let $t = qR$, $\beta = f/C$ and $\alpha = B/CR^2$. So the imaginary part of $\eta(t)$ is

$$\eta(t) = \frac{\beta}{t(1+\alpha t^2 V(t))}. \tag{7}$$

The Coulomb kernel $V(t) = 2K_0(t)I_0(t)$ asymptoticly goes to $1/t$ for large t and $const - 2\ln(t)$ for small t, i.e.

$$\lim_{t\to\infty}\eta(t) = \frac{\beta}{\alpha t^2} \tag{8}$$

$$\lim_{t\to 0}\eta(t) = \frac{\beta}{t} \tag{9}$$

Observe that

$$\eta(t) = \frac{\beta}{t(1+\alpha t)} \tag{10}$$

shows the same asymptotic behavior as Eq.7 for both large t and small t. Let's take the $\eta(t)$ in Eq.10 to be an ansatz and Fourier transform it. We get

$$\begin{aligned}
\eta(z) &= \frac{2}{\pi}\int_0^\infty dz \sin(tz)\mathrm{Im}\eta(t) \\
&= \frac{2}{\pi}\int_0^\infty \frac{\beta}{t(1+\alpha t)}\sin(tz)dz \\
&= \beta\,[(1-\cos(z') + 2/\pi Si(z')\cos(z')] \\
&\quad -2/\pi Ci(z')\sin(z')] \qquad (11)
\end{aligned}$$

where $z' = z/\alpha$. When $\alpha = 1$, the real space solution has a series form $(const - \ln(z))z + o(z^2)$ around $z = 0$ and $1 - 1/z + o(1/z^3)$ as z goes to infinity. The charge density can be derived

$$\begin{aligned}
\rho(z) &= -e\frac{\partial\eta(z)}{\partial z} \\
&= -e\frac{\beta}{\alpha}\,[\sin(z') - 2/\pi Si(z')\sin(z') \\
&\quad -2/\pi Ci(z')\cos(z')] \qquad (12)
\end{aligned}$$

Once we know how does the charge density vary along the tube, we can find the scaling of the bound charge in terms of a decay length. This can be calculated from the first moment of the charge density $Q_1 = \int_0^L \rho(z)zdz = \alpha^2\int_0^L \rho(z')z'dz'$ and the total charge $Q_0 = \int_0^L \rho(z)dz = \alpha\int_0^l \rho(z')dz'$. So the charge density length can be found from

$$\begin{aligned}
d &= \frac{Q_1}{Q_0} \qquad (13)\\
&= \alpha C1 \qquad (14)
\end{aligned}$$

where

$$C1 = \frac{\int_0^L \rho(z')z'dz'}{\int_0^L \rho(z')dz'}, \qquad (15)$$

Therefore, the spread of charge density scale with $\alpha = \frac{B}{CR^2}$.

To find out the potential drop between two points on the tube, we rewrite Eq.(2) into

$$\begin{aligned}
\eta(z) + \frac{f(z)}{C} &= \frac{e^2}{C}\int_0^L \frac{\partial V(z-z')}{\partial z}\frac{\partial\eta(z)}{\partial z'}dz' \qquad (16)\\
&= \frac{e^2}{C}\frac{\partial}{\partial z}\int_0^L V(z-z')\frac{\partial\eta(z)}{\partial z'}dz' \qquad (17)\\
&= \frac{e}{C}\frac{\partial U(z)}{\partial z} \qquad (18)
\end{aligned}$$

where $U(z)$ is the potential function. Therefore

$$U(z) = \frac{C}{e}\int_z^{L/2}(\eta(\xi) - \frac{f}{C})d\xi \qquad (19)$$

B. Fourier series solution

The Fourier series expansion of a periodic function on the interval of $[-L, L]$ is defined as

$$f(x) = \frac{a_0}{2} + \sum_n a_n\cos\frac{n\pi x}{L} + \sum_n b_n\sin\frac{n\pi x}{L} \qquad (20)$$

where

$$\begin{aligned}
a_0 &= \frac{1}{L}\int_{-L}^{L} f(x)dx \\
a_n &= \frac{1}{L}\int_{-L}^{L} f(x)\cos\frac{n\pi x}{L} \\
b_n &= \frac{1}{L}\int_{-L}^{L} f(x)\sin\frac{n\pi x}{L} \qquad (21)
\end{aligned}$$

To solve the problem, we define a periodical interval $[-M, M]$ on which the tube extends in the range of $[-L/2, L/2]$. $(L \leq M)$. Therefore, we can expand the Coulomb kernel $V(z-z')$ as

$$\begin{aligned}
V(z-z') &= \frac{A_0}{2} + \sum_{s,t} A_{s,t}\cos\frac{t\pi z}{M}\cos\frac{s\pi z'}{M} + \sum_{s,t} B_{s,t}\sin\frac{t\pi z}{M}\sin\frac{s\pi z'}{M} \\
&+ \sum_{s,t} C_{s,t}\sin\frac{t\pi z}{M}\cos\frac{t\pi z'}{M} + \sum_{s,t} D_{s,t}\cos\frac{t\pi z}{M}\sin\frac{s\pi z'}{M} \\
&+ \sum_t E_t\sin\frac{t\pi z}{M} + \sum_s F_s\sin\frac{s\pi z'}{M} \\
&+ \sum_t G_t\cos\frac{t\pi z}{M} + \sum_s H_s\cos\frac{s\pi z'}{M} \qquad (22)
\end{aligned}$$

where

$$A_0 = \frac{1}{M^2}\int_{-M}^{M}\int_{-M}^{M} V(z-z')dzdz' \tag{23}$$

$$A_{st} = \frac{1}{M^2}\int_{-M}^{M}\int_{-M}^{M} V(z-z')\cos\frac{t\pi}{M}z\cos\frac{s\pi}{M}z'dzdz' \tag{24}$$

and

$$B_{st} = \frac{1}{M^2}\int_{-M}^{M}\int_{-M}^{M} V(z-z')\sin\frac{t\pi}{M}z\sin\frac{s\pi}{M}z'dzdz' \tag{25}$$

Since we know that $\eta(z)$ is even, we can expand it using only the cosine series:

$$\eta(z) = \frac{a_0}{2} + \sum_n a_n \cos\frac{n\pi z}{M} \tag{26}$$

thus,

$$\begin{aligned} \eta'(z) &= \frac{d\eta(z)}{dz} \\ &= -\frac{\pi}{M}\sum_n n a_n \sin\frac{n\pi z}{M} \end{aligned} \tag{27}$$

The piezoelectric and elastic constant are defined as

$$\begin{gathered} e(z) = e(H(z+L/2) - H(z+L/2)) \\ C(z) = C(H(z+L/2) - H(z+L/2)) \end{gathered} \tag{28}$$

For a one flavor tube, the elastic energy becomes

$$\begin{aligned} &G_e \\ &= \frac{1}{2}C\int_{-L/2}^{L/2}\eta^2(z)dz \\ &= \frac{1}{2}C\int_{-L/2}^{L/2}\left(\frac{a_0}{2} + \sum_n a_n\cos\frac{n\pi z}{M}\right)^2 dz \\ &= \frac{Ca_0^2L}{8} + \frac{MC}{\pi}\sum_n \frac{a_0 a_n}{n}\sin n\alpha \\ &+ \frac{1}{2}C\sum_{nn'} a_n a_{n'} T_1(n,n') \end{aligned} \tag{29}$$

where

$$\begin{aligned} &T_1(n,n') \\ &= \int_{-L/2}^{L/2} dz\cos\frac{n\pi}{M}z\cos\frac{n'\pi}{M}z \\ &= \frac{2M}{\pi(n^2-n'^2)}(n\sin n\alpha\cos n'\alpha - n'\cos n\alpha\sin n'\alpha) \end{aligned} \tag{30}$$

and $\alpha = \frac{\pi L}{2M}$. In the special case that $n = n'$,

$$T_1(n,n) = \frac{M}{\pi}\frac{\cos n\alpha\sin n\alpha}{n} + \frac{L}{2} \tag{31}$$

The Coulomb energy term are separated into "bulk" term G_c^1, "edge" G_c^2 and "corner" term G_c^3 which are expressed in the following:

$$\begin{aligned} G_c^1 &= \frac{1}{2}e^2\int_{-L/2}^{L/2}\int_{-L/2}^{L/2}\frac{\partial\eta(z)}{\partial z}V(z-z')\frac{\partial\eta(z)}{\partial z}dzdz' \\ &= \frac{1}{2}e^2\frac{\pi^2}{M^2}\sum_{nn'} a_n a_{n'} nn' \sum_{st} B_{st} T_2(n,n',t,s) \end{aligned} \tag{32}$$

where

$$\begin{aligned} &T_2(n,n',s,t) \\ &= \int_{-L/2}^{L/2}\int_{-L/2}^{L/2} dzdz'\sin\frac{n\pi}{M}z\sin\frac{n'\pi}{M}z'\sin\frac{t\pi}{M}z\sin\frac{s\pi}{M}z' \\ &= T_3(n,t)T_3(n',s) \end{aligned} \tag{33}$$

and

$$\begin{aligned} &T_3(n,t) \\ &= \int_{-L/2}^{L/2} dz'\sin\frac{n\pi}{M}z'\sin\frac{t\pi}{M}z' \\ &= 2\frac{M}{\pi(n^2-t^2)}\left[-n\cos n\alpha\sin t\alpha + t\sin n\alpha\cos t\alpha\right] \end{aligned} \tag{34}$$

The edge term is

$$\begin{aligned} G_c^2 &= e^2\int\left[\eta(-L/2)V(-L/2-z')\eta'(z')\right. \\ &- \left.\eta(L/2)V(L/2-z')\eta(z')\right]dz' \end{aligned} \tag{35}$$

where

$$\begin{aligned}
&\eta(-L/2)\int_{-L/2}^{L/2} V(-L/2-z')\eta'(z')dz' \\
&= \frac{\pi}{M}\eta(-L/2)\sum_{n'} n' a_{n'} \sum_s (\sum_t (-B_{ts}\sin t\alpha + D_{ts}\cos t\alpha) + F_s)\int_{-L/2}^{L/2} \sin\frac{s\pi}{M}z'(-\sin\frac{n'\pi}{M}z')dz' \\
&= -\frac{\pi}{M}\eta(-L/2)\sum_{n'} n' a_{n'} \sum_s (\sum_t (-B_{ts}\sin t\alpha + D_{ts}\cos t\alpha) + F_s)T_3(s,n') \qquad (36)
\end{aligned}$$

Therefore

$$G_c^2 = -2e^2\frac{\pi}{M}\eta(-L/2)\sum_{n'} n' a_{n'} \sum_s (\sum_t (-B_{ts}\sin t\alpha + D_{ts}\cos t\alpha) + F_s)T_3(s,n') \qquad (37)$$

and the "corner" term is

$$\begin{aligned}
G_c^3 &= \frac{1}{2}e^2\int_{-L/2}^{L/2}\int_{-L/2}^{L/2}(\delta(z+L/2)-\delta(L/2-z))\eta(z)V(z-z')(\delta(z+L/2)-\delta(L/2-z'))\eta(z')dzdz' \\
&= \frac{1}{2}e^2\eta(-L/2)V(0)\eta(-L/2) - \eta(-L/2)V(L)\eta(L/2) - \eta(L/2)V(L)\eta(-L/2) + \eta(L/2)V(0)\eta(L/2) \\
&= e^2\eta(L/2)^2(V(0)-V(L)) \qquad (38)
\end{aligned}$$

We define an external force to be

$$f(z) = f(H(z+L/2) - H(z-L/2)) \qquad (39)$$

therefore, the "distortion" term is equal to

$$\begin{aligned}
G_{ext} &= -f\int_{-L/2}^{L/2}\eta(z)dz \\
&= -\frac{fa_0L}{2} - 2\frac{fM}{\pi}\sum_n \frac{a_n}{n}\sin n\alpha \qquad (40)
\end{aligned}$$

It can be seen that we need the constraint $\eta(L/2) = \eta(-L/2) = 0$ to keep the free energy finite. Therefore $a_0 = -2\sum a_n\cos n\alpha$. Substitute the constraint back into the energies, G_c^2 and G_c^3 should vanish, the elastic energy becomes

$$\begin{aligned}
G_e &= \frac{1}{2}CL(\sum_n a_n\cos n\alpha)^2 - 2\frac{MC}{\pi}\sum_{nn'}\frac{a_{n'}a_n}{n}\cos n\alpha\sin n\alpha \\
&+ \frac{1}{2}C\sum_{nn'} a_n a_{n'} T_1(n,n') \qquad (41)
\end{aligned}$$

and the distortion term

$$G_{ext} = fL\sum_n a_n\cos n\alpha - 2\frac{fM}{\pi}\sum_n\frac{a_n}{n}\sin n\alpha. \qquad (42)$$

Now we can write the free energy as

$$G = G_e + G_c^1 + G_c^2 + G_c^3 + G_{ext} \qquad (43)$$

and we want to minimize G over the Fourier coefficients a_n. To do that, we solve a set of linear equations $Q\vec{a} = P$. From

$$\begin{aligned}
\frac{\partial G}{\partial a_i} &= CL\cos i\alpha\sum_{n'} a_{n'}\cos n'\alpha - \frac{2MC}{\pi}(\cos i\alpha\sum_n\frac{a_n}{n}\sin n\alpha + \frac{\sin i\alpha}{i}\sum_{n'} a_{n'}\cos n'\alpha) \\
&+ C\sum_n a_n T_1(i,n) + e^2\frac{\pi^2}{M^2}i\sum_n n a_n\sum_{st} B_{st}T_2(i,n,t,s) + fL\cos i\alpha - \frac{2fM}{\pi}\frac{\sin i\alpha}{i}, \qquad (44)
\end{aligned}$$

we get the left hand matrix Q

$$\begin{aligned}
Q_{ij} &= \frac{\partial^2 G}{\partial a_i\partial a_j} \\
&= CL\cos i\alpha\cos j\alpha - \frac{2MC}{\pi}(\frac{\cos i\alpha\sin j\alpha}{j} + \frac{\sin i\alpha\cos j\alpha}{i})
\end{aligned}$$

and the right hand side vector P is

$$P_i = -fL\cos i\alpha + \frac{2fM}{\pi}\frac{\sin i\alpha}{i} \qquad (46)$$

Because the Coulomb potential is actually not periodic, we actually don't need to worry about the periodic images and therefore we should take $M = L/2$ for all the calculations.

From the solution of

$$\eta(z) = \frac{a_0}{2} + \sum_n a_n \cos\frac{2n\pi z}{L} \tag{47}$$

we can calculate the charge density,

$$\begin{aligned} \rho_\alpha(z) &= -e_\alpha \frac{\partial \eta_\alpha}{\partial z} \\ &= \frac{2e_\alpha \pi}{L}\sum_n n a_n \sin\frac{2n\pi z}{L} \end{aligned} \tag{48}$$

where $\alpha = s$ or t for a one flavor tube. And the total charge from the boundary to the middle of the tube

$$\begin{aligned} Q &= \int_{-L/2}^{0} \rho_\alpha(z) dz \\ &= -e \sum_n a_n \cos\frac{2n\pi z}{L}\Big|_{-L/2}^{0} \\ &= -e(\sum_n a_n - \sum_n a_n \cos n\alpha) \\ &= -e(\frac{a_0}{2} + \sum_n a_n) = -e\eta(0) \end{aligned} \tag{49}$$

The first moment of charge density is

$$\begin{aligned} Q^{(1)} &= \int_{-L/2}^{0} (L/2 + z)\rho_\alpha(z) dz \\ &= L/2 * Q + \frac{2e\pi}{L}\sum_n n a_n \int_{-L/2}^{0} \sin\frac{2n\pi z}{L} z dz \\ &= L/2 * Q + \frac{2e\pi}{L}\sum_n n a_n \left[-\frac{L^2}{4n^2\pi^2} n\pi \cos n\pi\right] \\ &= L/2 * Q + -\frac{eL}{2}\sum_n a_n \cos n\pi \\ &= L/2 * Q + \frac{eL}{4} a_0 \end{aligned} \tag{50}$$

therefore, the "half width" of the charge density can be measure as

$$d = \frac{Q^{(1)}}{Q} = \frac{L}{2} - \frac{L}{4}\frac{a_0}{\eta(0)}. \tag{51}$$

The electric potential becomes

$$\begin{aligned} \phi(z) &= \int \rho(z') V(z - z') dz' \\ &= \frac{2e_\alpha \pi}{L}\sum_n n a_n \int V(z - z') \sin\frac{2n\pi z'}{L} dz' \end{aligned} \tag{52}$$

and the corresponding electric field becomes

$$\begin{aligned} \mathcal{E}(z) &= -\frac{\partial \phi(z)}{\partial z} \\ &= -\int \rho(z')\frac{\partial V(z - z')}{\partial z} dz' \\ &= -\frac{2e_\alpha \pi}{L}\sum_n n a_n \int \frac{\partial V(z - z')}{\partial z} \sin\frac{2n\pi z'}{L} dz' \\ &= \frac{4e_\alpha \pi^2}{L^2}\sum_n n^2 a_n \int V(z - z') \cos\frac{2n\pi z'}{L} dz' \end{aligned} \tag{53}$$

II. RESULT

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[1] N. Sai, E.J. Mele Phys. Rev. B Rapid Comm 2003.