

Supporting Information for
Enhanced Electro-actuation in Dielectric Elastomers:
The Nonlinear Effect of Free Ions

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1. The Free Energy

The free energy is written as,

$$\begin{aligned} \frac{F_{\text{elec}}}{k_{\text{B}}T} = \int d^3r \left\{ -\frac{1}{8\pi l_{\text{B}}}(\nabla\Psi)^2 + (c_+ - c_-)\Psi \right. \\ \left. -\tilde{\mu}_+c_+ - \tilde{\mu}_-c_- + c_+\ln(c_+a_+^3) + c_-\ln(c_-a_-^3) \right. \\ \left. + a_{\text{gel}}^{-3}(1 - c_+a_+^3 - c_-a_-^3)\ln(1 - c_+a_+^3 - c_-a_-^3) \right\}. \end{aligned} \quad (1)$$

The first two terms account for the electrostatic energy, where $l_{\text{B}} = e^2/(4\pi\epsilon_0\epsilon_r k_{\text{B}}T)$ is the Bjerrum length, ϵ_r is the dielectric constant of the gel in the absence of ions, and $\Psi = e\psi/k_{\text{B}}T$ is the dimensionless electrostatic potential. The third and fourth terms account for the chemical potential of the free ions, where $\tilde{\mu}_{\pm} = \mu_{\pm}/k_{\text{B}}T$ is the dimensionless chemical potential and $c_{\pm}(r)$ is the cation and anion number density. Because the thickness of the gel film, L , is large, the film is considered to be coupled to a bulk reservoir (inner film) of free ions via the ion chemical potential, $\tilde{\mu}_{\pm}$. The fifth and sixth terms are the entropy of the cations and anions. Finally, the last term in Eq. (1) is the entropy of the gel molecules acting as a solvent. This solvent entropy is responsible for the saturation effect of the free ions that accumulate near the electrodes.^{1,2}

Under large electric fields, due to the anion saturation at the gel/anode interface, the amount of cations and solvent molecules at the anode is negligible. Similarly, the amount of the anions and solvent molecules is negligible at the gel/cathode interface. For convenience purposes only, we can then decouple the last term in Eq. (1) and write it as the sum of two separated steric terms. In addition, the gel size a_{gel} is taken the same as the size of the dominant ion respectively. The first term contributes only at the cathode, while the second one contributes only at the anode.

$$\begin{aligned} \frac{F_{\text{elec}}}{k_{\text{B}}T} = \int d^3r \left\{ -\frac{1}{8\pi l_{\text{B}}}(\nabla\Psi)^2 + (c_+ - c_-)\Psi \right. \\ \left. -\tilde{\mu}_+c_+ - \tilde{\mu}_-c_- + c_+\ln(c_+a_+^3) + c_-\ln(c_-a_-^3) \right. \\ \left. + a_+^{-3}(1 - c_+a_+^3)\ln(1 - c_+a_+^3) + a_-^{-3}(1 - c_-a_-^3)\ln(1 - c_-a_-^3) \right\}. \end{aligned} \quad (2)$$

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2. The Ion Distribution and Electrostatic Potential inside the PVC Gel

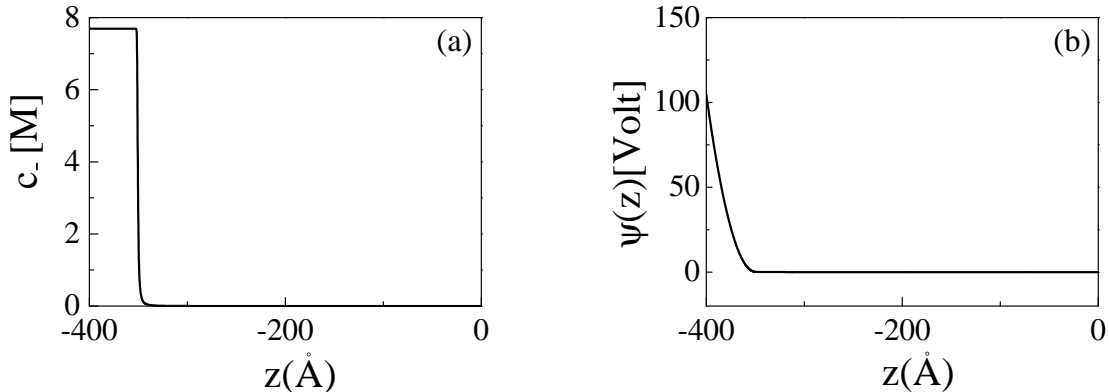


FIG. 1. Electrostatic profiles for half of the system (anode side) as a function of z , the distance measured from the mid-plane between the electrodes. The anode is located at $z = -L/2 = -400 \text{ \AA}$. The anion distribution and electrostatic potential are plotted, respectively, in (a) and (b). The other parameters are $\eta = 2.0$, $\Delta S/S_0 = 0.115$, $(\bar{S} - S_0)/S_0 = 0.241$, $q_0 = Q/S_0 = 0.3 \text{ \AA}^{-2}$, $a_+ = 3 \text{ \AA}$, and $c_b = 1 \text{ mM}$.

The numerical results presented in Fig. 1 show that anions are closely packed on the anode side with a number density $c_- = 1/a_-^3$. As a result, there are almost no cations in that region. Correspondingly, there are closely packed cations and no anions on the cathode side. This is due to the high voltage (electric field on the order of 1 kV/mm) applied across the electrodes. We assume charge neutrality of the entire system, *i.e.*, the total amount of the anions (cations) in the gel is equal to the charge number on the anode (cathode). As a result, we can estimate the thickness of the close-packed charge layer to be $L_e^+ = q_+ a_-^3$.

3. Dielectric Constant

The other interesting behavior of the PVC gel is its large apparent dielectric constant, ε_{app} , which is about $10^3 - 10^4$ times larger than the dielectric constant of the PVC and the embedded plasticizer.³ We show how the free ions play a crucial role in explaining this intriguing behavior.

To estimate the apparent dielectric constant, we model the system as a two-plate capacitor of thickness L . Around each electrode there is an electric double-layer of thickness L_e^\pm coupled with the inner film of thickness $L - (L_e^+ + L_e^-)$. We assume that the surface charge-densities on the electrodes is $\pm q$. Thus, we can use the following relation for the

capacitance,

$$C = eq \frac{S}{V} = \varepsilon_0 \varepsilon_{\text{app}} \frac{S}{L}, \quad (3)$$

where the applied voltage $V = V_e + V_b$ has two contributions: a bulk part, V_b , and an electric double-layer part, V_e . And V can be approximately written as

$$V = V_e + E_b L_b \approx \frac{1}{2} E_0 (L_e^+ + L_e^-) + E_b L, \quad (4)$$

where L_e^\pm was shown to be the electric double-layer thickness and $L_b = L - (L_e^+ + L_e^-)$ is the inner film thickness. The electric field in the bulk is denoted as E_b , while $E_0 \equiv eq/(\varepsilon_0 \varepsilon_r)$ is the bulk electric field in the absence of free ions inside the gel. From Eqs. (3) and (4), we obtain an explicit expression of the apparent dielectric constant, ε_{app} ,

$$\frac{1}{\varepsilon_{\text{app}}} \simeq \frac{1}{\varepsilon_r} \left(\frac{L_e^+ + L_e^-}{2L} + \frac{E_b}{E_0} \right). \quad (5)$$

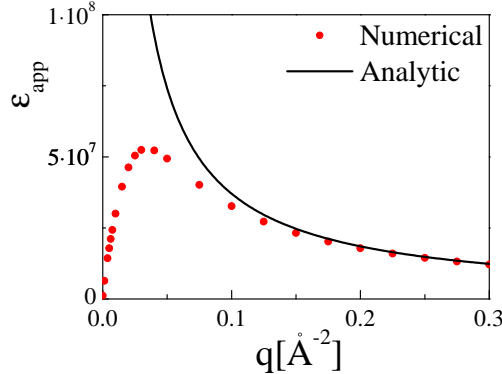


FIG. 2. The apparent dielectric constant ε_{app} as a function of the surface charge density, $q = Q/S$ on a semi-log plot. The other parameters are $c_b = 1\text{mM}$, $a_\pm = 3\text{\AA}$, $L = 1\text{mm}$ and $\varepsilon_r = 10$.

Equation (5) shows that indeed such free ions are at the origin of this special dielectric behavior. When there are no free ions, $\varepsilon_{\text{app}} = \varepsilon_r$, where ε_r includes the plasticizer and PVC contributions. The large ε_{app} values occur only when free ions are added, leading to a significant reduction of the bulk electric field, E_b . Moreover, the increase of the film thickness L leads to a large apparent dielectric constant, ε_{app} .

We further estimate the value of ε_{app} by ignoring the bulk electric field ($E_b = 0$). For small q near 0, the electric double-layer thickness L_e^\pm is of the order of the Debye length λ_D . Then $\varepsilon_{\text{app}} \simeq \varepsilon_r L / \lambda_D$ is independent of q and is much larger than ε_r . For large q , $L_e^\pm = qa_\pm^3$

and V_e is obtained from the explicit expression of $\Psi(z)$, Eq. (7) in the paper.

$$\frac{eV_e}{k_B T} = 2\pi l_B q^2 (a_-^3 + a_+^3), \quad (6)$$

yielding an approximate analytical expression of

$$\varepsilon_{\text{app}} = 2\varepsilon_r L (a_-^3 + a_+^3)^{-1} q^{-1}. \quad (7)$$

The dependence of ε_{app} on the surface charge-density q is shown in Fig. 2. When the surface charge-density q increases gradually from zero, the apparent dielectric constant ε_{app} first increases, reaching a maximum that is followed by a decrease.

REFERENCES

- [1] Borukhov, I.; Andelman, D.; Orland, H. Steric Effects in Electrolytes: A Modified Poisson-Boltzmann Equation. *Phys. Rev. Lett.* **1997**, 79, 435-438.
- [2] Borukhov, I.; Andelman, D.; Orland, H. Adsorption of Large Ions from An Electrolyte Solution: A Modified Poisson-Boltzmann Equation. *Electrochim. Acta* **2000**, 46, 221-229.
- [3] Ali, M.; Ueki, T.; Tsurumi, D.; Hirai, T. Influence of Plasticizer Content on the Transition of Electromechanical Behavior of PVC Gel Actuator. *Langmuir* **2011**, 27, 7902-7908.