Materials for soft machines

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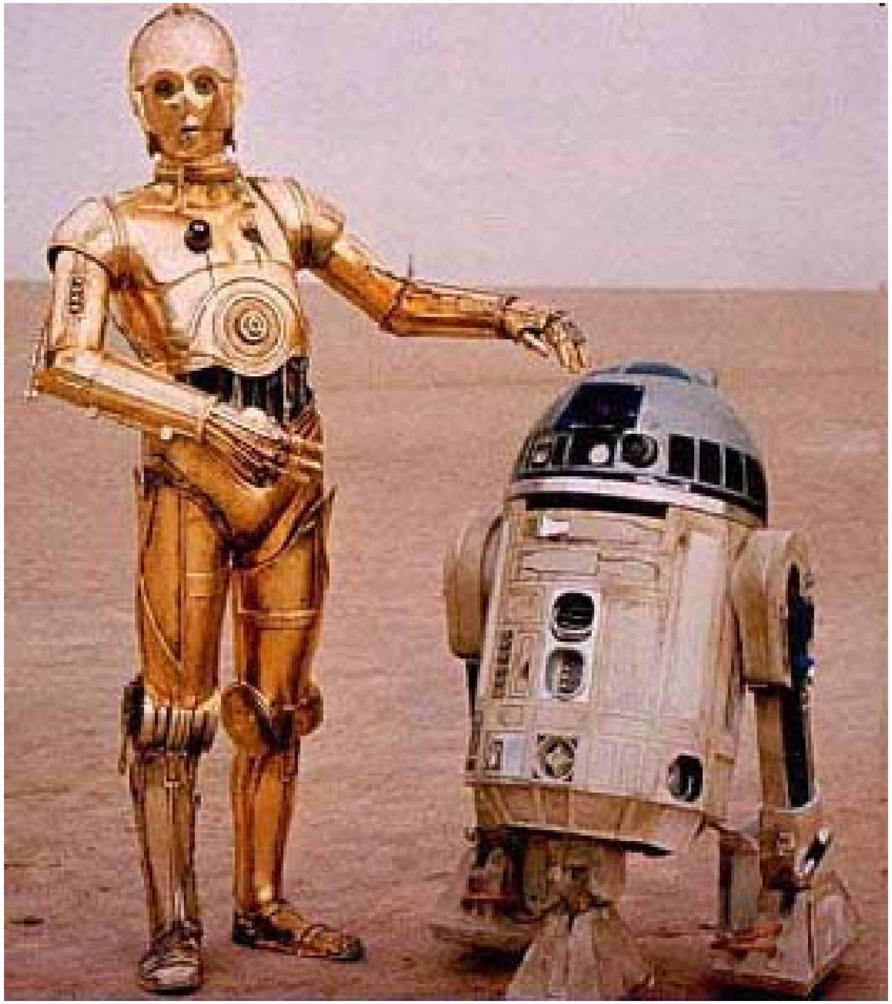
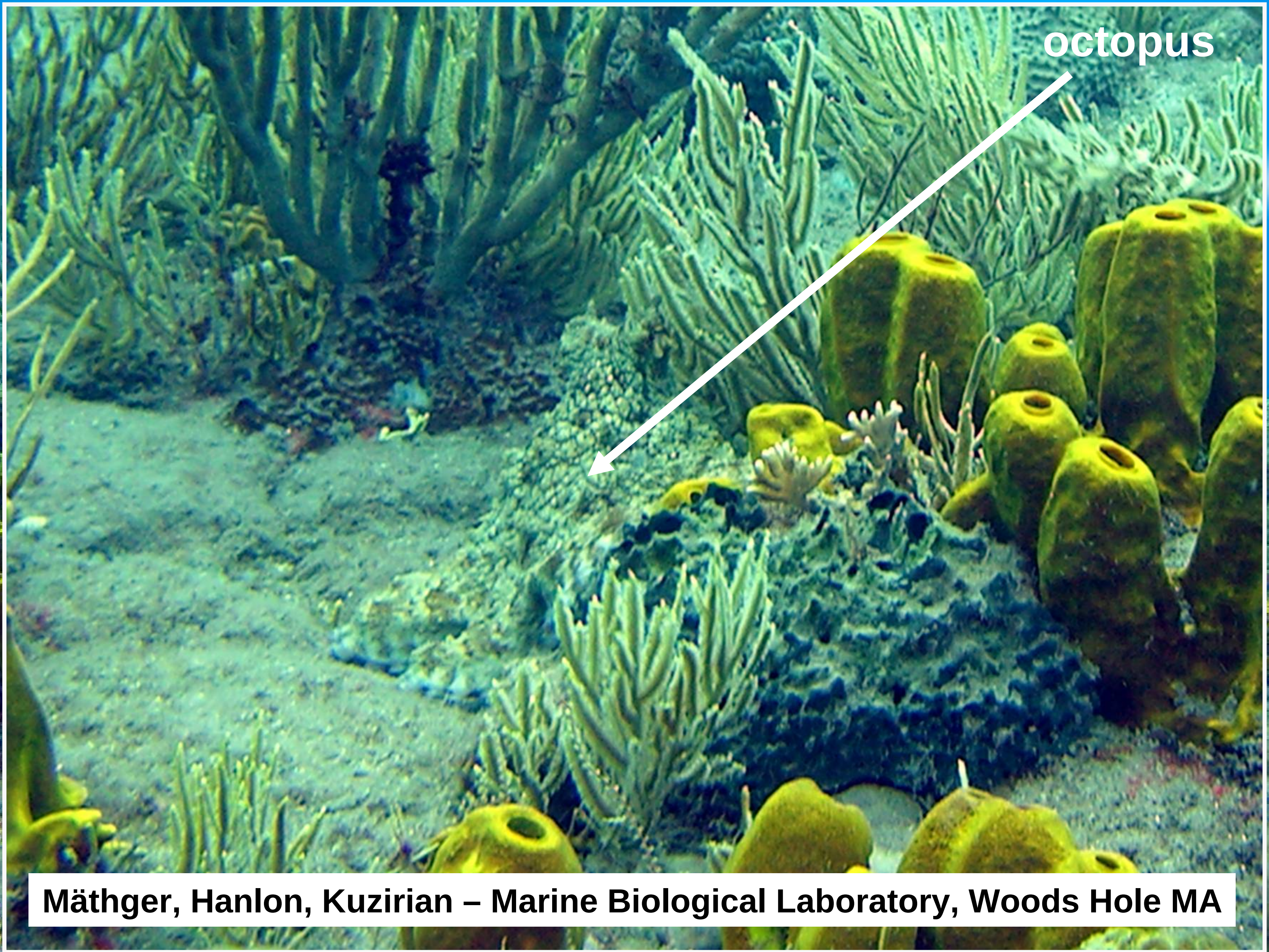
Harvard University

Hard Machines

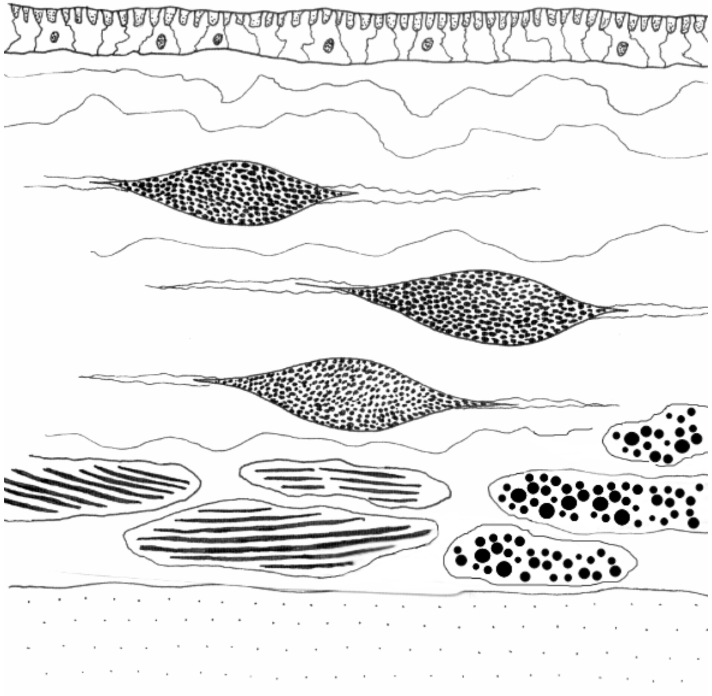


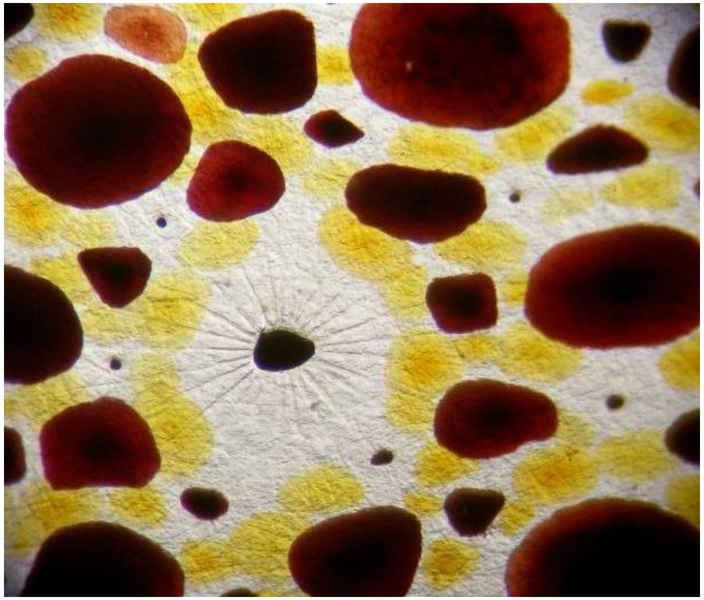
Soft Machines


octopus
Mäthger, Hanlon, Kuzirian – Marine Biological Laboratory, Woods Hole MA

Squid changes color

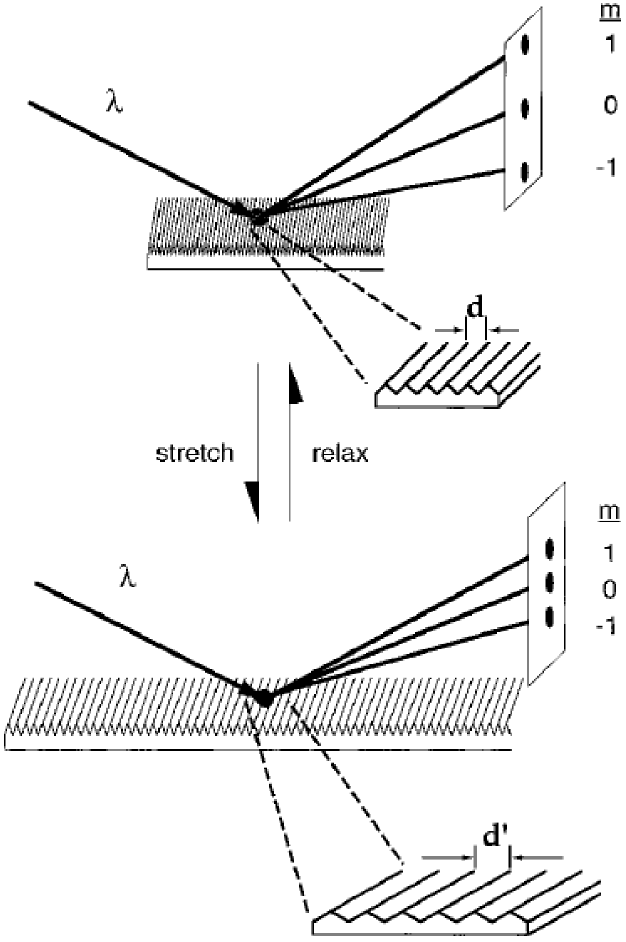
Expanding chromatophores by contracting radial muscles



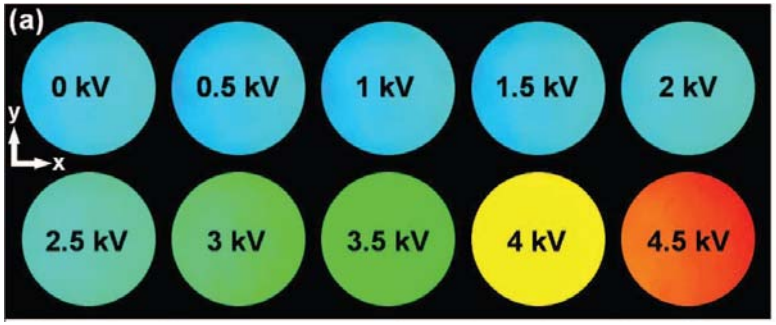


Mathger, Denton, Marshall, Hanlon, J. R. Soc. Interface 6, S149 (2009)

Adaptive Optics



•Many stimuli cause deformation.
•Deformation affects optics.

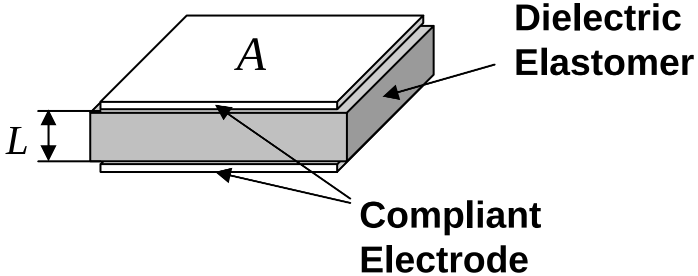


Wilbur, Jackman, Whitesides, Cheung, Lee, Prentiss
Elastomeric optics
Chem. Mater. 1996, 8, 1380-1385

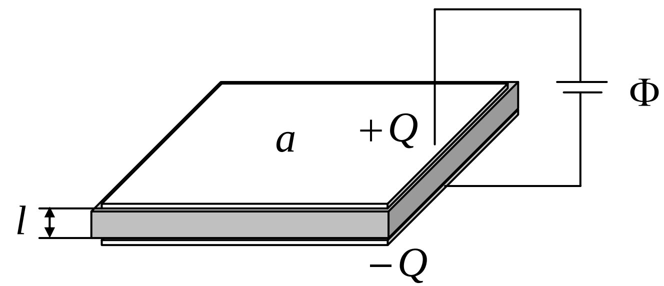
Aschwanden, Stemmer
Optics letters 31, 2610 (2006)

Dielectric elastomer

Reference State

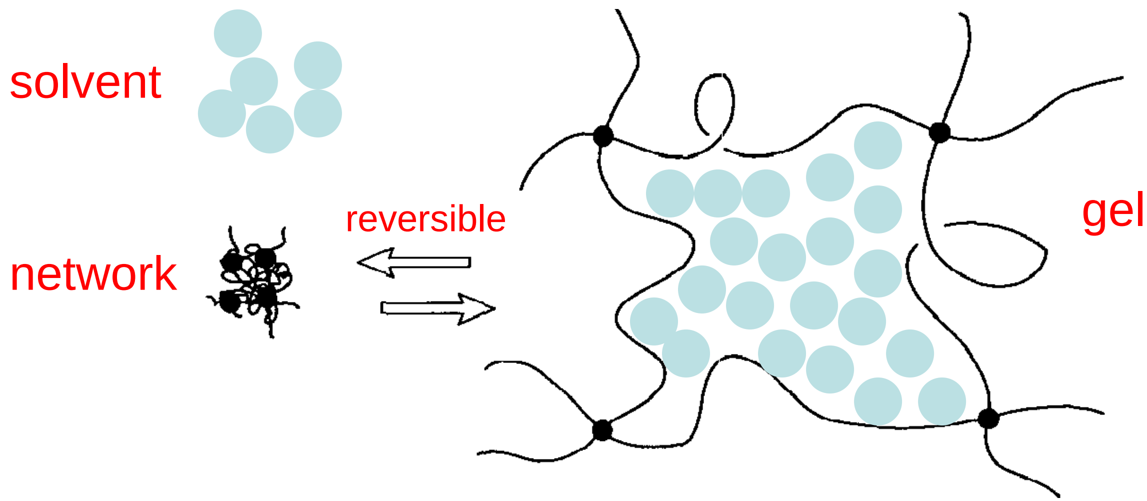


Current State

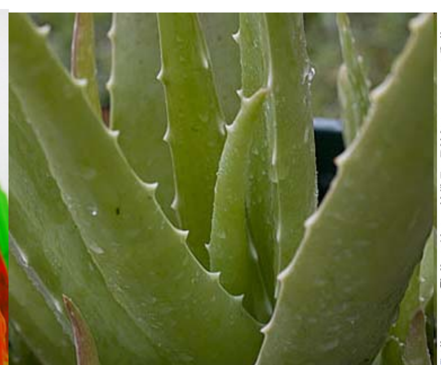


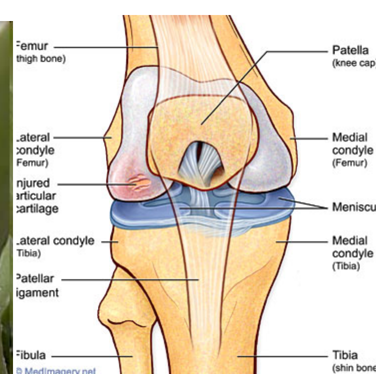
Pelrine, Kornbluh, Pei, Joseph
High-speed electrically actuated elastomers with strain greater than 100%.
Science 287, 836 (2000).

gel = network + solvent

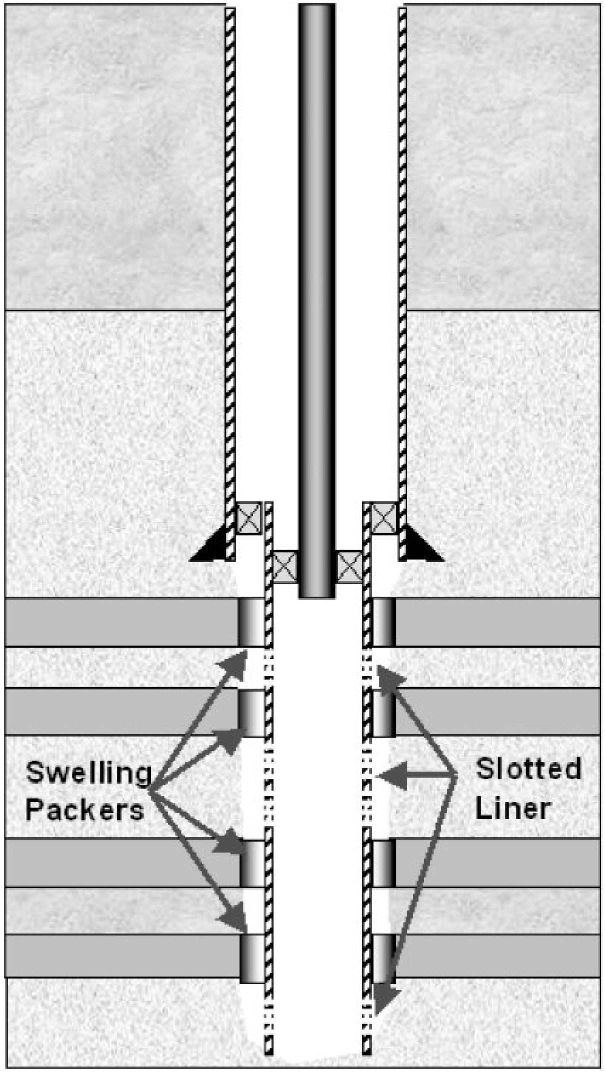


Solid-like: long polymers crosslink by strong bonds. Retain shape
Liquid like: polymers and solvent aggregate by weak bonds. Enable transport





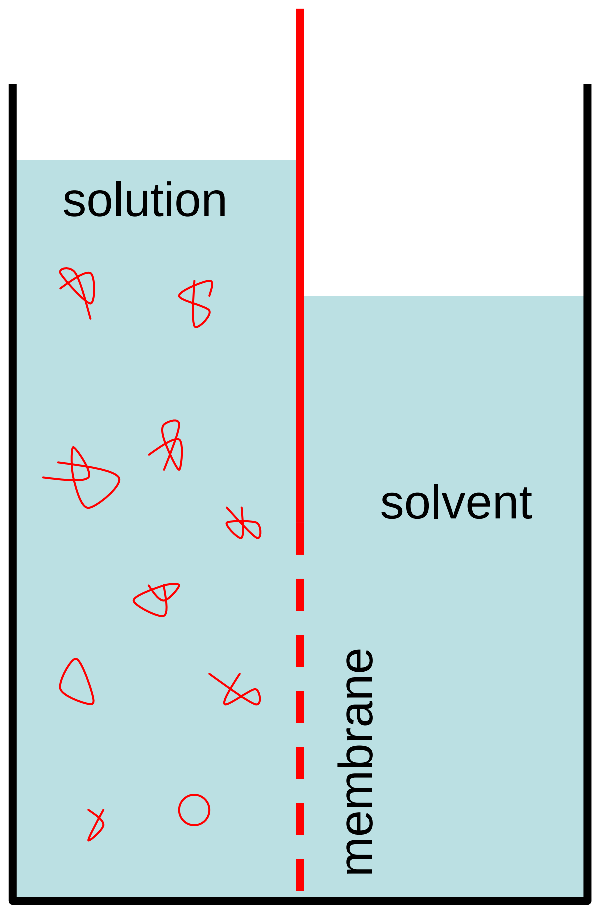
Swelling packers in oil wells



A project with Schlumberger

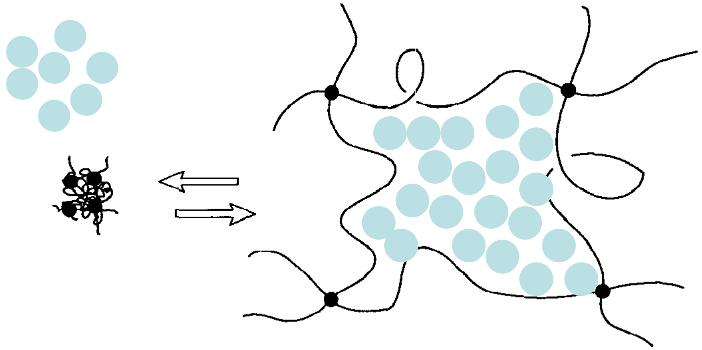
Osmosis

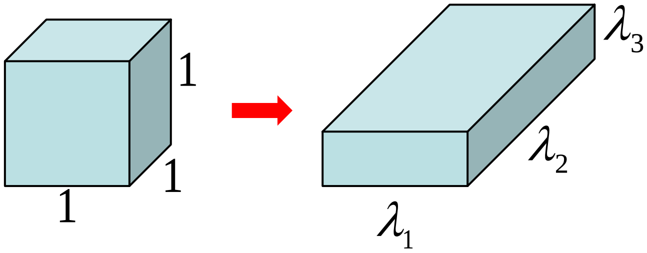
$$\Pi = ckT$$



Neutral gel

Paul Flory





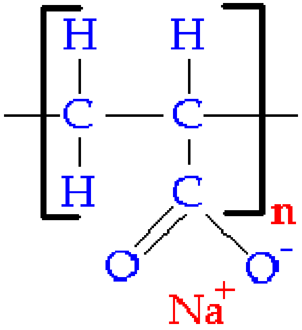
$$\sigma_1 = \frac{NkT}{\lambda_2 \lambda_3}\left(\lambda_1 + \frac{1}{\lambda_1}\right) - \Pi_{sol}$$

$$\Pi_{sol} = -\frac{kT}{v_S}\left\{\log\left(1 - \frac{1}{\lambda_1\lambda_2\lambda_3}\right) + \frac{1}{\lambda_1\lambda_2\lambda_3} + \frac{\chi}{(\lambda_1\lambda_2\lambda_3)^2}\right\}$$

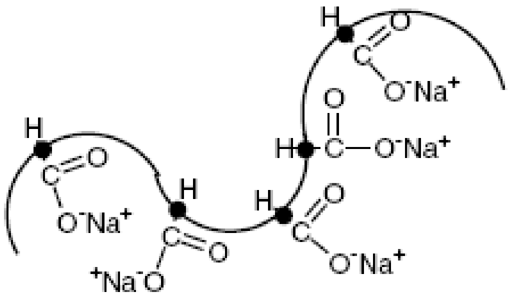
Flory, Rehner, J. Chem. Phys., 11, 521 (1943)

Diaper

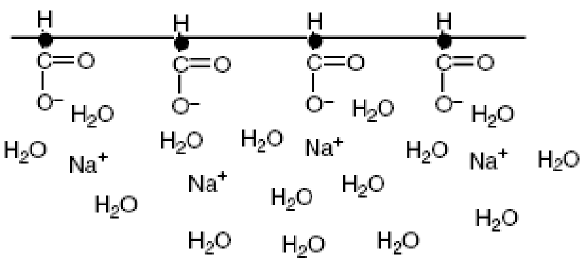
Sodium polyacrylate



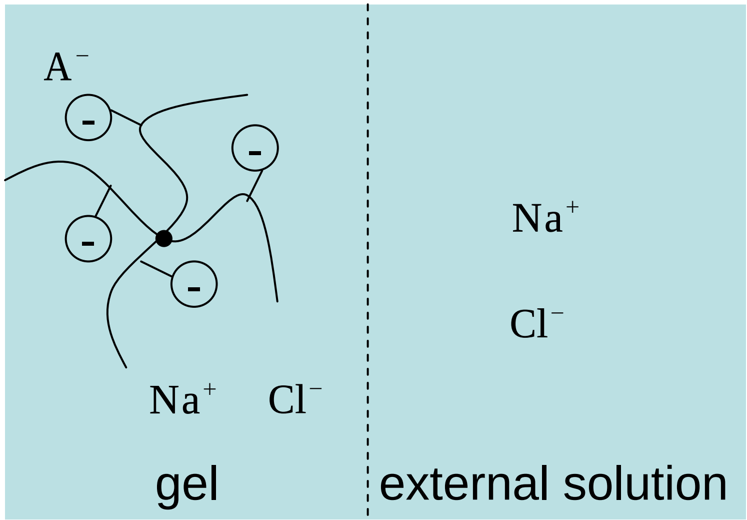
Dry



in Water



Super Absorption



Electroneutrality

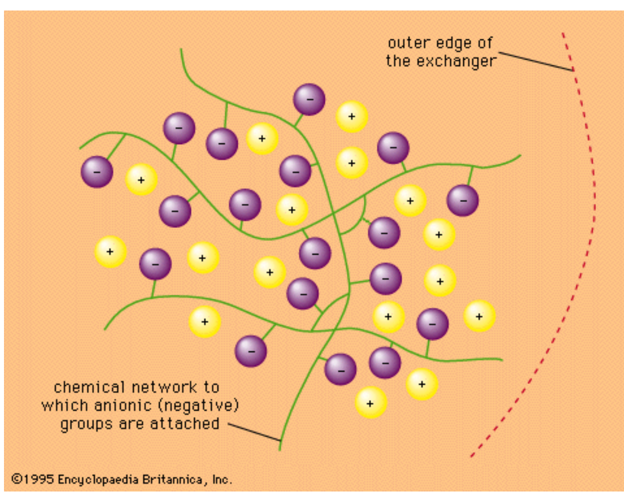
$$[Na^+]_{gel} = [Cl^-]_{gel} + [A^-]_{gel} \qquad [Na^+]_{ext} = [Cl^-]_{ext}$$

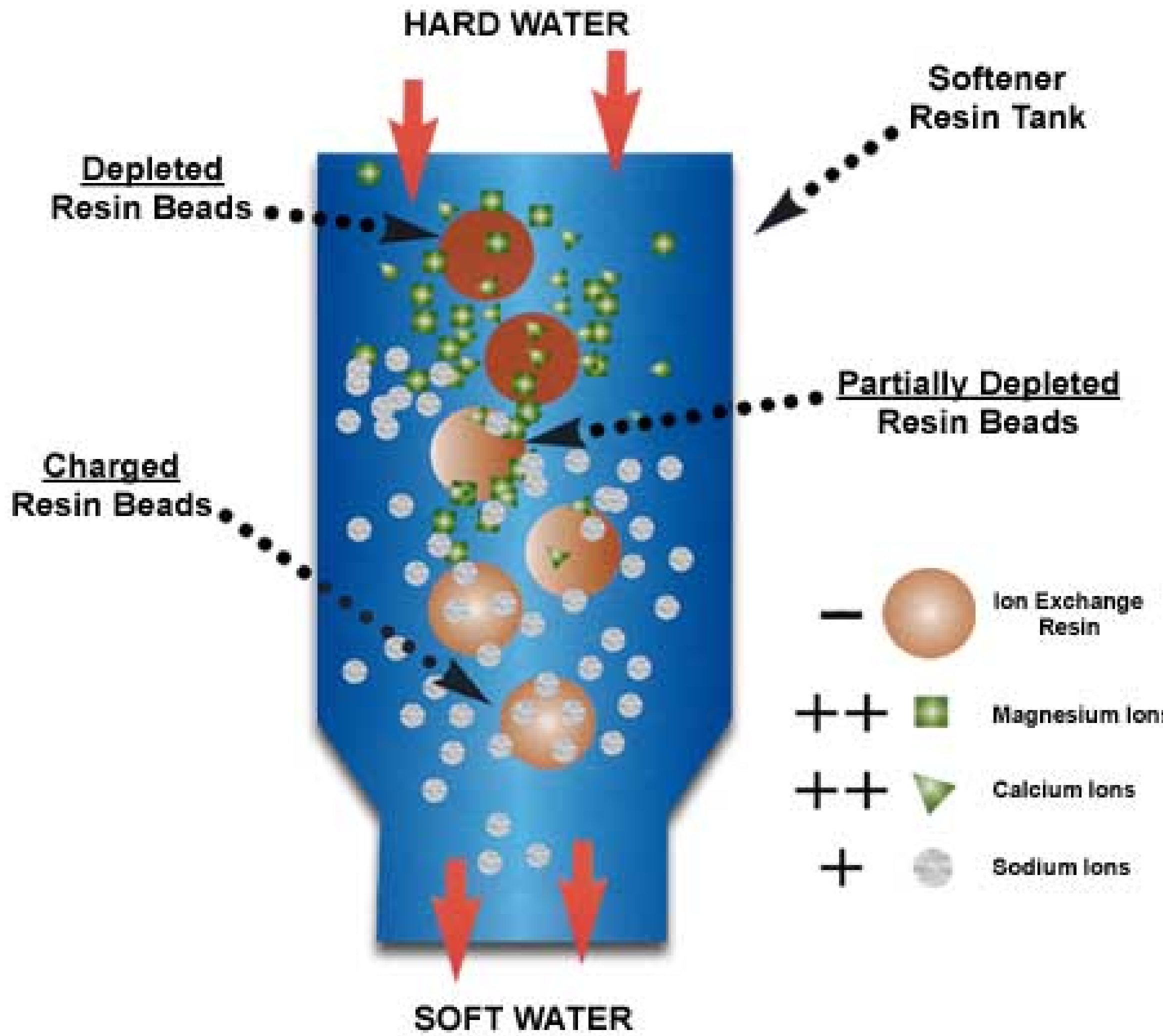
Donnan equilibrium

$$[Na^+]_{gel}[Cl^-]_{gel} = [Na^+]_{ext}[Cl^-]_{ext}$$

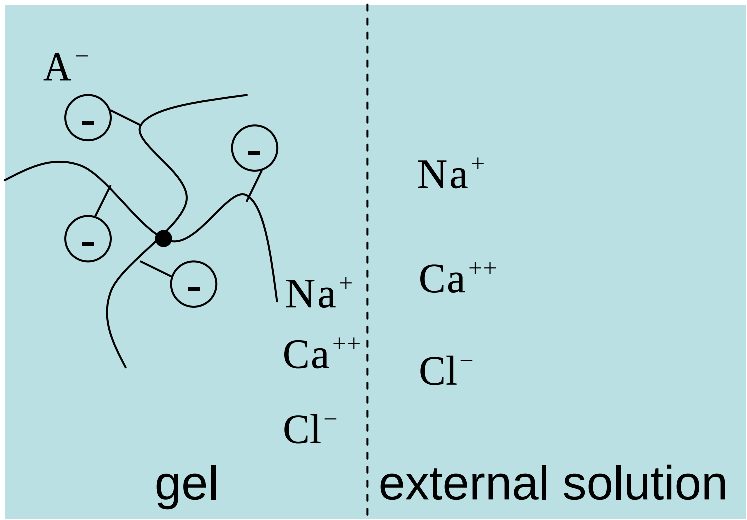
Ion exchanger

$$XNa_2 + Ca^{++} \rightarrow XCa + 2Na^{+}$$





Ion exchange

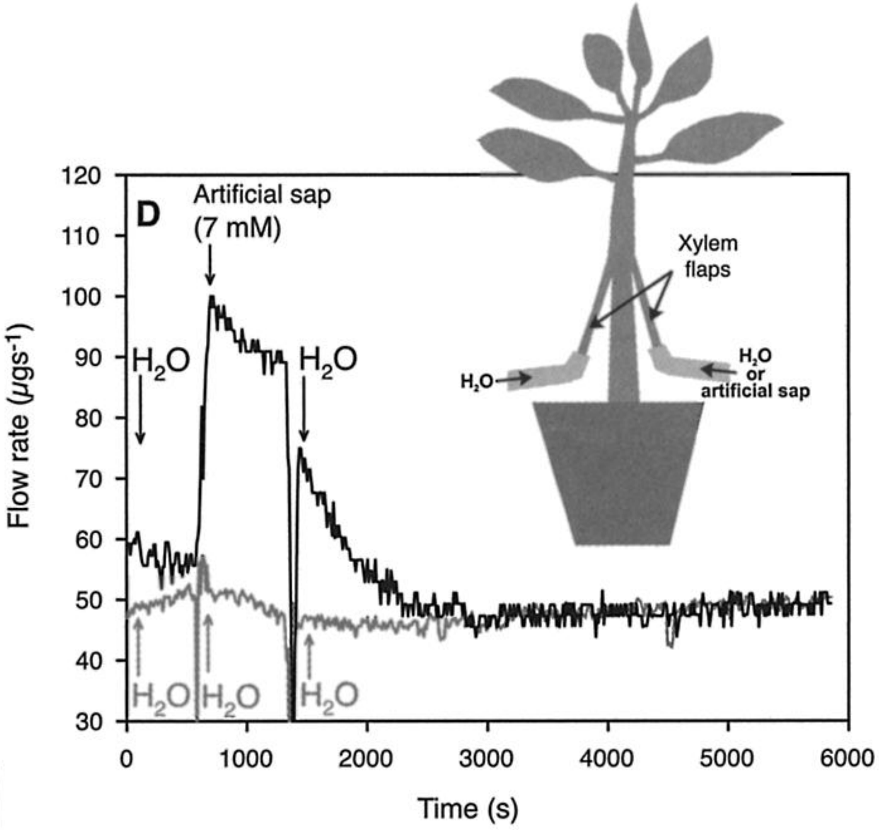


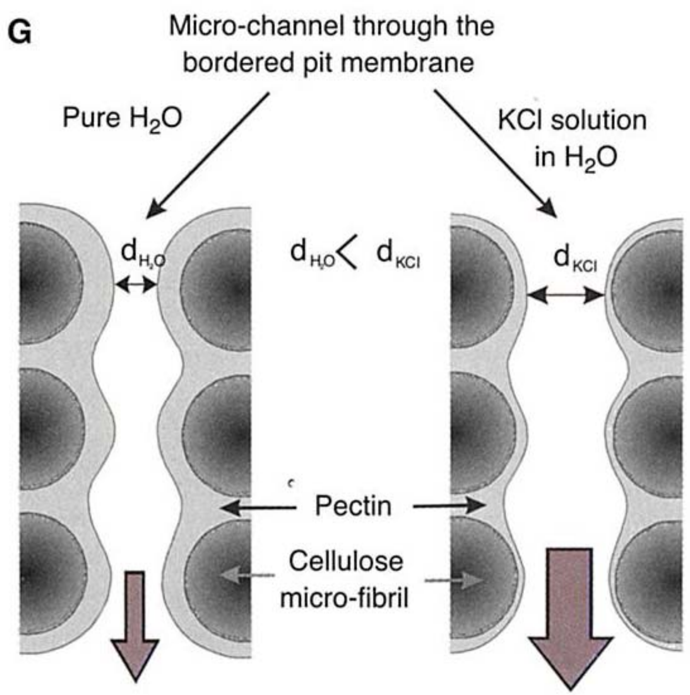
Donnan equilibrium

$$\frac{\left[Ca^{++}\right]_{gel}}{\left[Ca^{++}\right]_{ext}} = \left(\frac{\left[Na^{+}\right]_{gel}}{\left[Na^{+}\right]_{ext}}\right)^2$$

Gels regulate flow in plants

Missy Holbrook

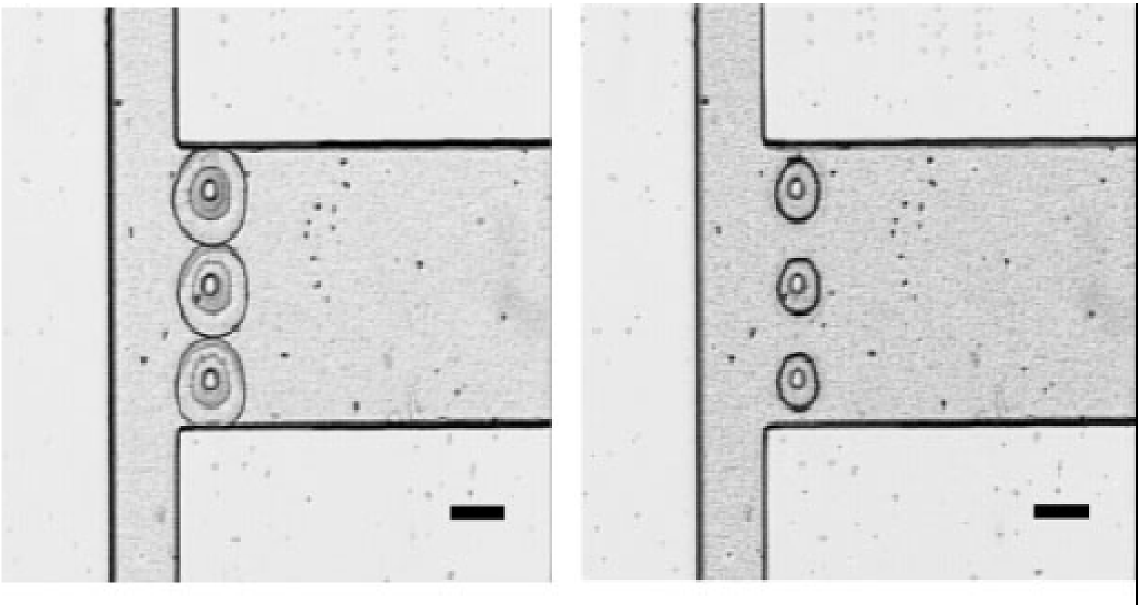




Zwieniecki, Melcher, Holbrook,
Hydrogel control of xylem hydraulic resistance in plants
Science 291, 1095 (2001)

Self-regulating fluidics

David Beebe



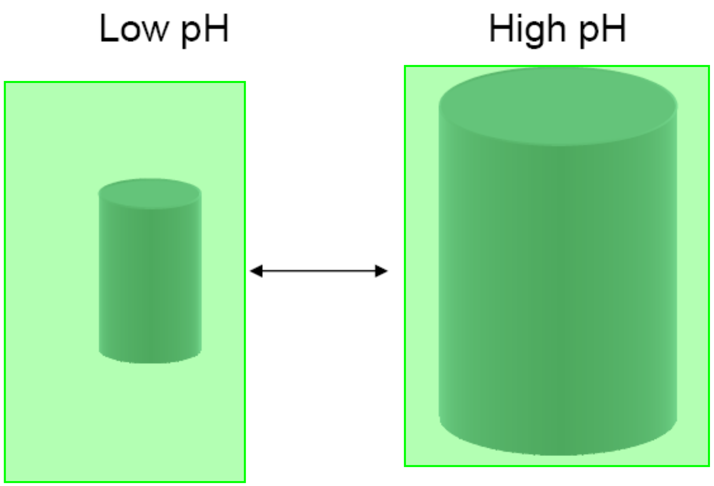
Responsive to Physiological variables:

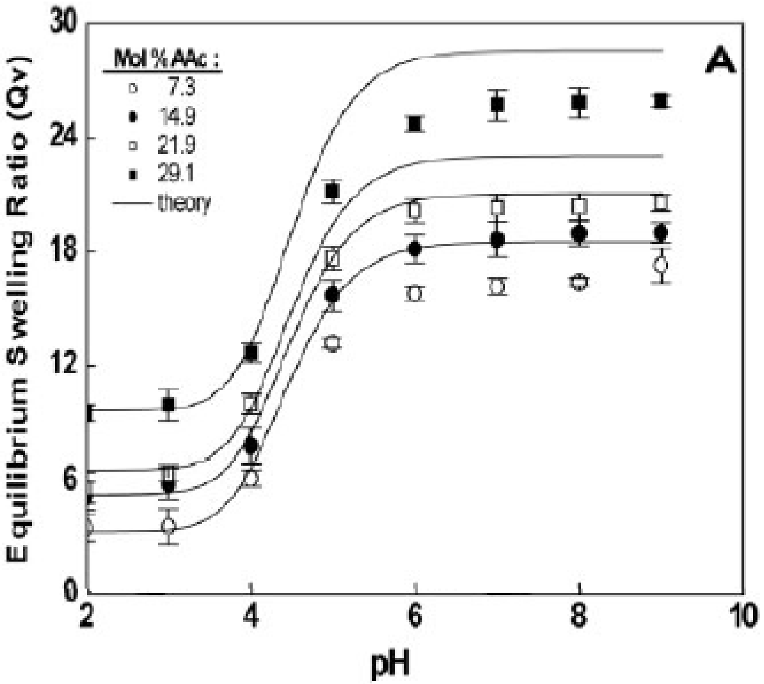
- •pH
- •Salt
- •Temperature
- •light

•Many stimuli cause deformation.
•Deformation affects flow.

Beebe, Moore, Bauer, Yu, Liu, Devadoss, Jo, Nature 404, 588 (2000)

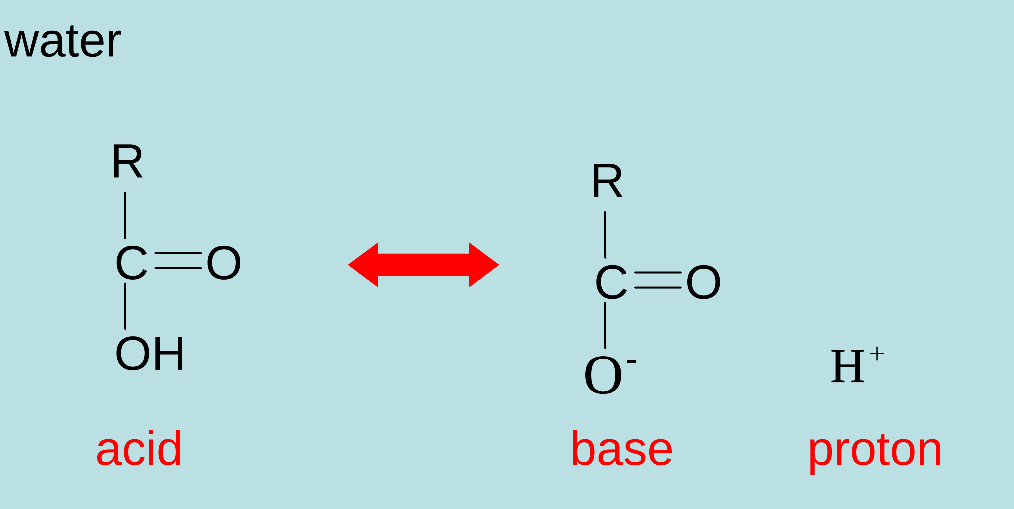
pH-sensitive hydrogel





$$\mathrm{pH} = -\log_{10}\left[\mathrm{H}^{+}\right]$$

Dissociation of an acid

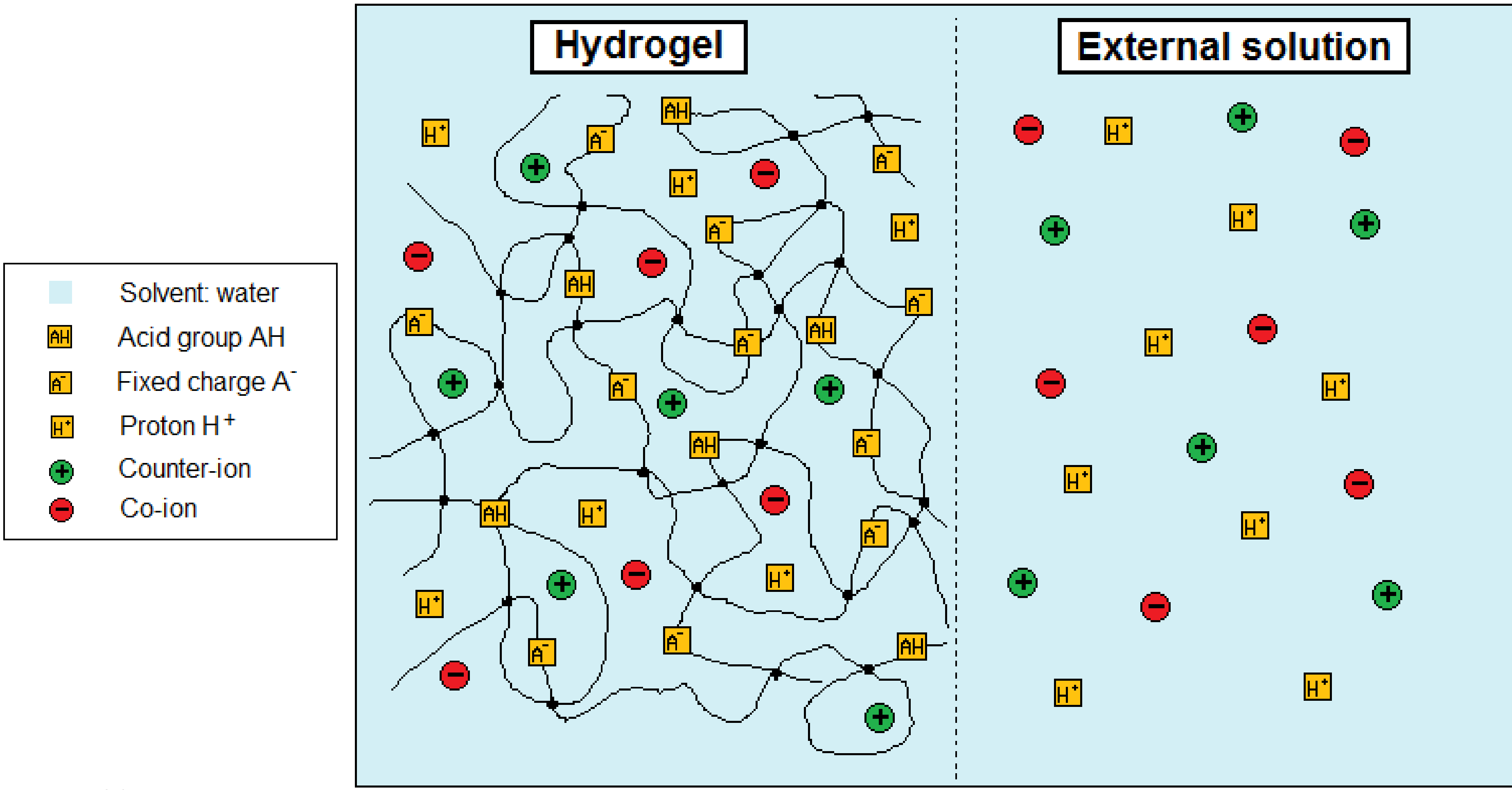


$$\mathrm{RCOOH} \Leftrightarrow \mathrm{RCOO}^{-} + \mathrm{H}^{+}$$

$$\frac{[\mathrm{RCOO}^{-}][\mathrm{H}^{+}]}{[\mathrm{RCOOH}]} = K$$

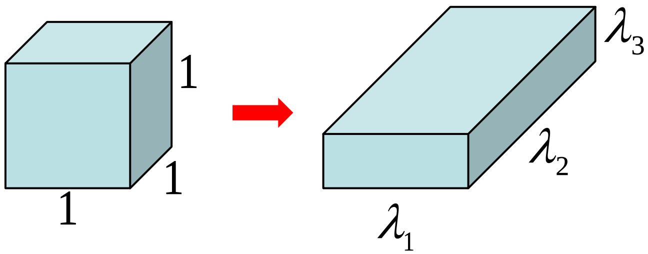
Constant of acidic dissociation

pH-sensitive hydrogel



$$\sigma_1 = \frac{NkT}{\lambda_2\lambda_3}\left(\lambda_1 + \frac{1}{\lambda_1}\right) - \left(\Pi_{sol} + \Pi_{ion}\right)$$

$$\Pi_{sol} = -\frac{kT}{v_S}\left\{\log\left(1 - \frac{1}{\lambda_1\lambda_2\lambda_3}\right) + \frac{1}{\lambda_1\lambda_2\lambda_3} + \frac{\chi}{\left(\lambda_1\lambda_2\lambda_3\right)^2}\right\}$$



$$\Pi_{ion} = kT\left(c_{\mathrm{H}^+} + c_+ + c_- - \bar{c}_{\mathrm{H}^+} - \bar{c}_+ - \bar{c}_-\right)$$

Donnan equilibrium

$$c_+ / \bar{c}_+ = c_{\mathrm{H}^+} / \bar{c}_{\mathrm{H}^+} \qquad c_- / \bar{c}_- = \left(c_{\mathrm{H}^+} / \bar{c}_{\mathrm{H}^+}\right)^{-1}$$

Electroneutrality

$$c_+ + c_{\mathrm{H}^+} = c_- + c_{A^-}$$

Conservation of particles

$$c_{AH} + c_{A^-} = \frac{f}{v\lambda_1\lambda_2\lambda_3}$$

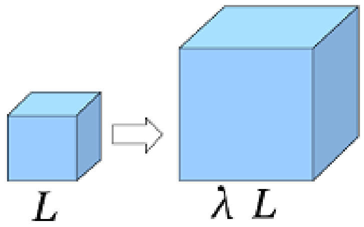
Constant of acidic dissociation

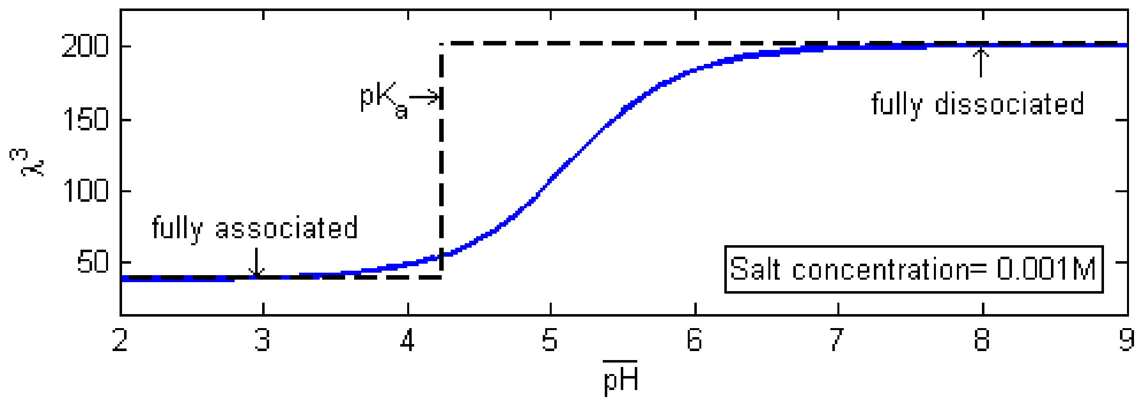
$$\frac{c_{A^-}c_{\mathrm{H}^+}}{c_{AH}} = N_A K$$

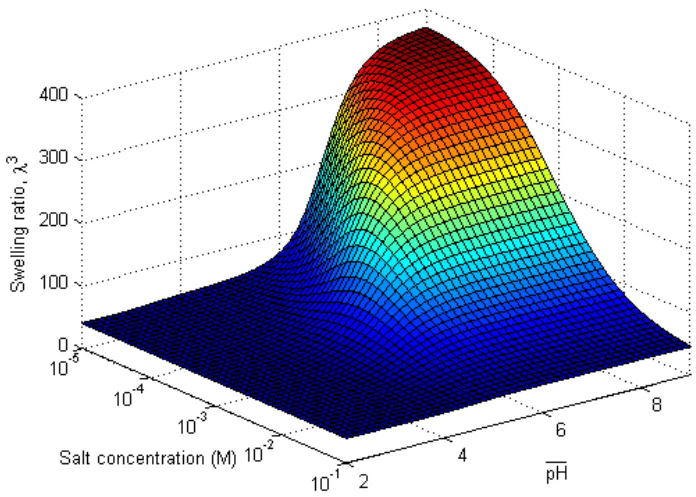
Ricka, Tanaka,Macromolecules17, 2916 (1984).

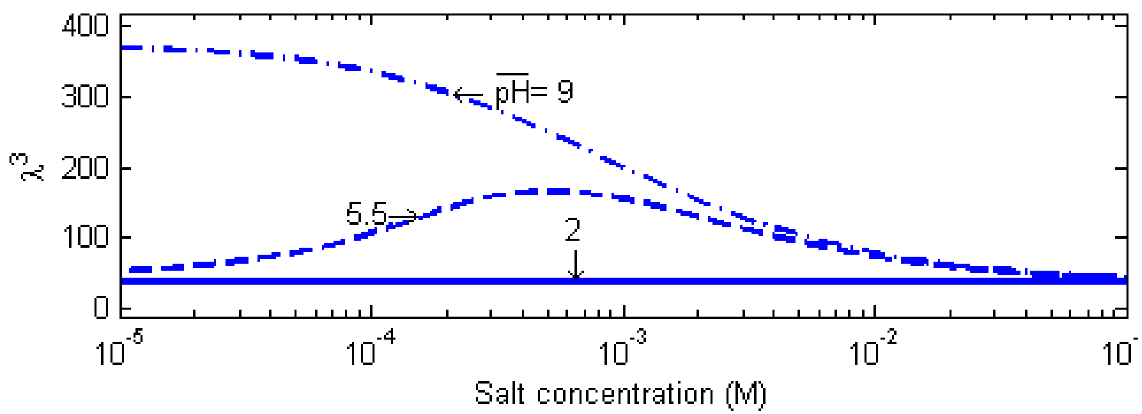
Marcombe, Cai, Wei, Zhao, Lapusta, Suo, Submitted

Free swelling

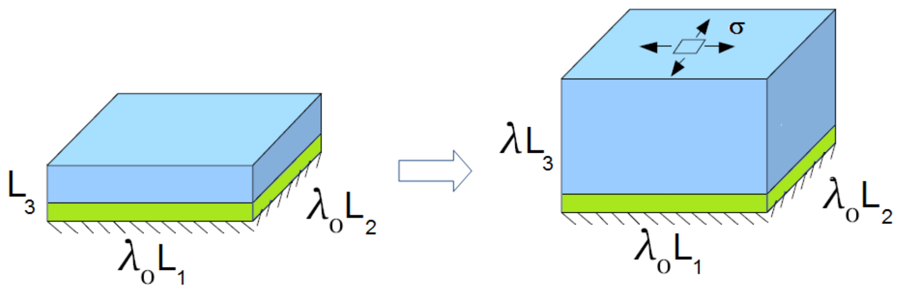


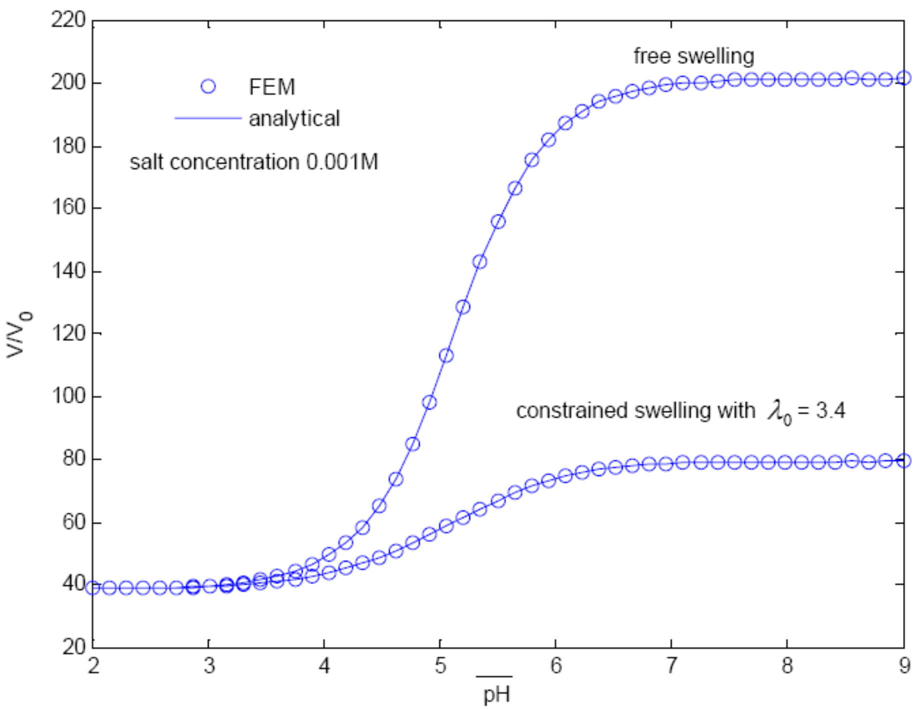




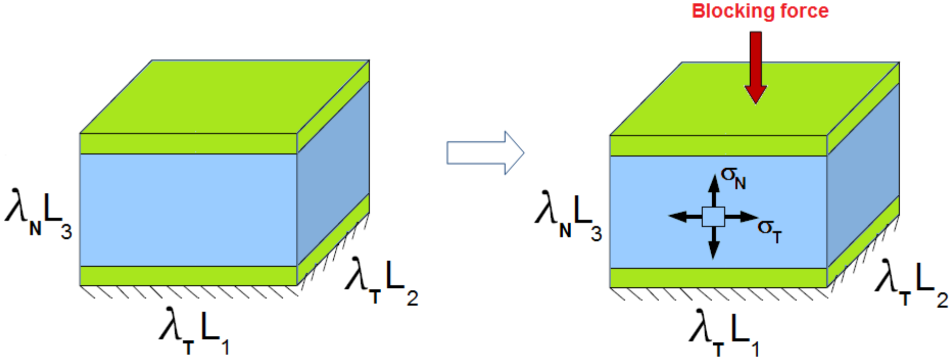


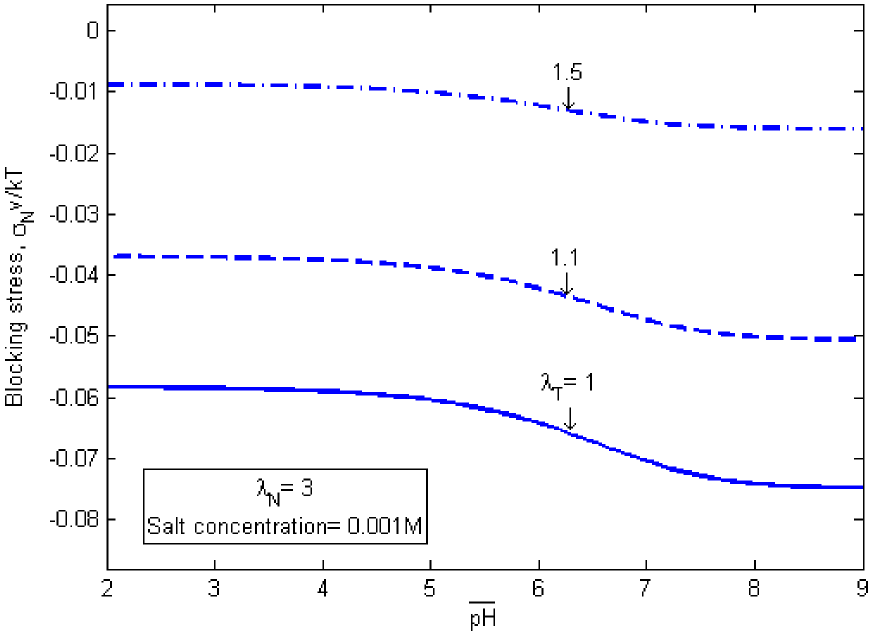
Constrained swelling





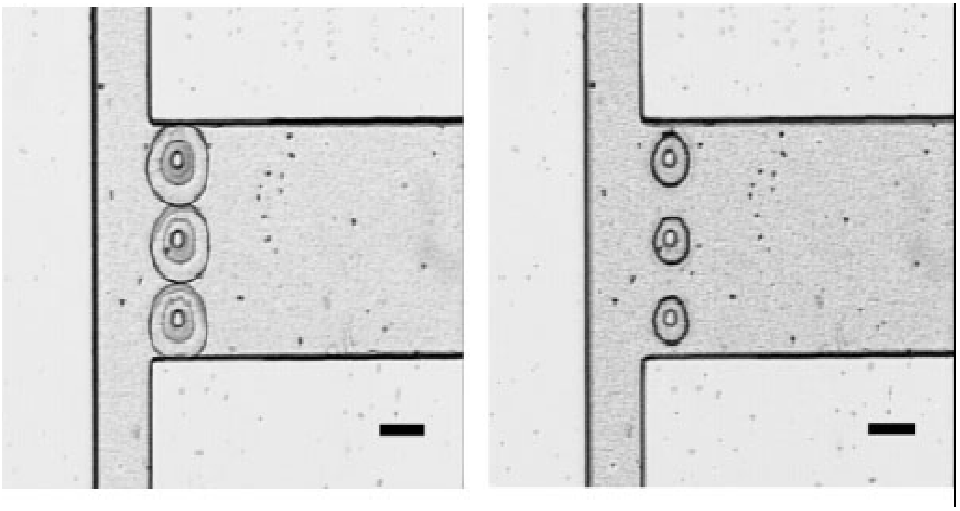
Blocking force





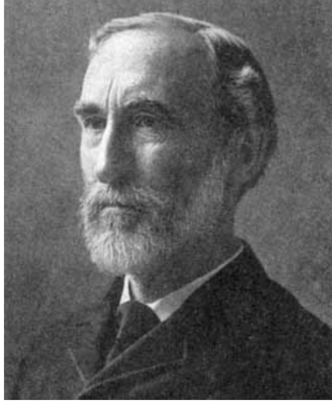
Inhomogeneous deformation

Swelling gels blocked by hard materials

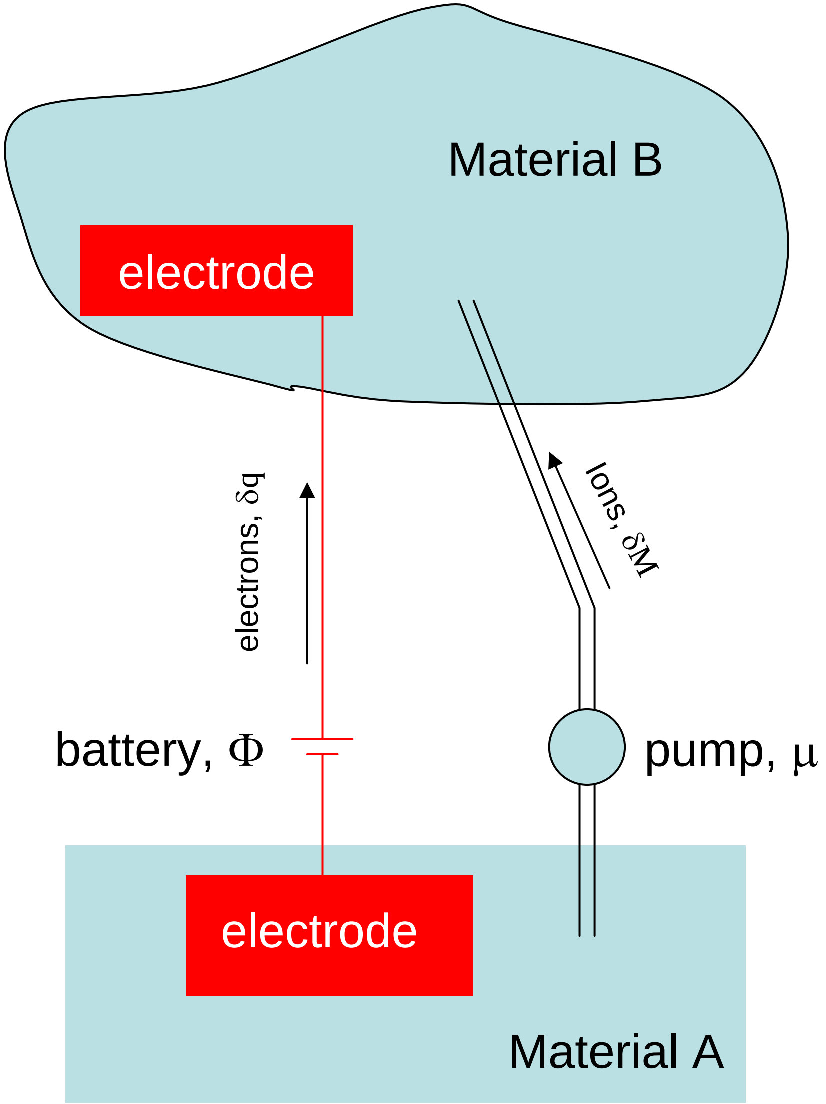


Need to formulate boundary-value problems

Electric potential
Electrochemical potential



Gibbs (1878)



- Battery does work on electrons, $\Phi\delta q$
- Pump does work on ions, $\mu\delta M$
- Helmholtz free energy of system, F

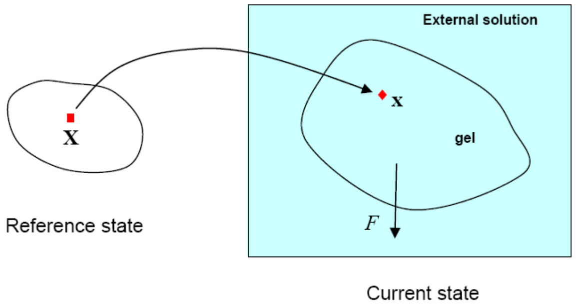
equilibrium $\delta F = \Phi\,\delta q + \mu\delta M$

electroneutrality $\delta q + ez\,\delta M = 0$

$$\delta F = \left(-ez\Phi + \mu\right)\delta M$$

$$\boxed{\mu = ez\Phi + \frac{\partial F}{\partial M}}$$

General principles



Deformation gradient $$F_{iK} = \frac{\partial x_i(\mathbf{X})}{\partial X_K}$$

Adding volumes $$1 + v_S C_S = \det \mathbf{F}$$

Electroneutrality $$C_{\mathrm{H}^+}(\mathbf{X}) + C_+(\mathbf{X}) = C_{\mathrm{A}^-}(\mathbf{X}) + C_-(\mathbf{X}) \qquad \bar{n}_{\mathrm{H}^+} + \bar{n}_+ = \bar{n}_-$$

Conservation of particles

$$\boxed{\begin{array}{l} \int \delta C_+(\mathbf{X}) dV + \delta \bar{n}_+ = 0 \qquad \int \delta C_S(\mathbf{X}) dV + \delta \bar{n}_S = 0 \qquad \int \delta C_-(\mathbf{X}) dV + \delta \bar{n}_- = 0 \\ \int \delta C_{\mathrm{H}^+}(\mathbf{X}) dV + \delta \bar{n}_{\mathrm{H}^+} = \int \delta C_{\mathrm{A}^-}(\mathbf{X}) dV \qquad C_{\mathrm{AH}}(\mathbf{X}) + C_{\mathrm{A}^-}(\mathbf{X}) = f / v \end{array}}$$

Independent variables $x_i(\mathbf{X})$, $C_+(\mathbf{X})$, $C_-(\mathbf{X})$, and $C_{\mathrm{H}^+}(\mathbf{X})$

Free energy function $W = W\left(\mathbf{F}, C_+, C_-, C_{\mathrm{H}^+}\right)$

Condition of equilibrium $$\int \delta W dV + \mu_S \delta \bar{n}_S + \mu_{\mathrm{H}^+} \delta \bar{n}_{\mathrm{H}^+} + \mu_+ \delta \bar{n}_+ + \mu_- \delta \bar{n}_- = \int B_i \delta x_i dV + \int T_i \delta x_i dA$$

Material model

Free energy of the gel

$$W = W_{net} + W_{sol} + W_{ion} + W_{dis}$$

$$W_{net} = \frac{1}{2} NkT\left[F_{iK}F_{iK} - 3 - 2\log(\det \mathbf{F})\right]$$

$$W_{sol} = \frac{kT}{v_S}\left[(\det \mathbf{F} - 1)\log\left(1 - \frac{1}{\det \mathbf{F}}\right) - \frac{\chi}{\det \mathbf{F}}\right]$$

$$W_{ion} = kT\left[C_{\mathrm{H}^+}\left(\log\frac{C_{\mathrm{H}^+}}{c_{\mathrm{H}^+}^{ref}\det \mathbf{F}} - 1\right) + C_+\left(\log\frac{C_+}{c_+^{ref}\det \mathbf{F}} - 1\right) + C_-\left(\log\frac{C_-}{c_-^{ref}\det \mathbf{F}} - 1\right)\right]$$

$$W_{dis} = kT\left[C_{\mathrm{A}^-}\log\left(\frac{C_{\mathrm{A}^-}}{C_{\mathrm{A}^-} + C_{\mathrm{AH}}}\right) + C_{\mathrm{AH}}\log\left(\frac{C_{\mathrm{AH}}}{C_{\mathrm{A}^-} + C_{\mathrm{AH}}}\right)\right] + \gamma C_{A^-}$$

Electrochemical potentials of particles in the external solution

$$\mu_+ - \mu_{\mathrm{H}^+} = kT\log\left(\frac{\bar{c}_+ c_{\mathrm{H}^+}^{ref}}{c_+^{ref}\bar{c}_{\mathrm{H}^+}}\right) \qquad \mu_- + \mu_{\mathrm{H}^+} = kT\log\left(\frac{\bar{c}_-\bar{c}_{\mathrm{H}^+}}{c_-^{ref}c_{\mathrm{H}^+}^{ref}}\right) \qquad \mu_S = -kTv_S\left(\bar{c}_{\mathrm{H}^+} + \bar{c}_+ + \bar{c}_-\right)$$

Finite element method

Condition of equilibrium $\int \delta W dV + \mu_S \delta \overline{n}_S + \mu_{H^+} \delta \overline{n}_{H^+} + \mu_+ \delta \overline{n}_+ + \mu_- \delta \overline{n}_- = \int B_i \delta x_i dV - \int T_i \delta x_i dA$

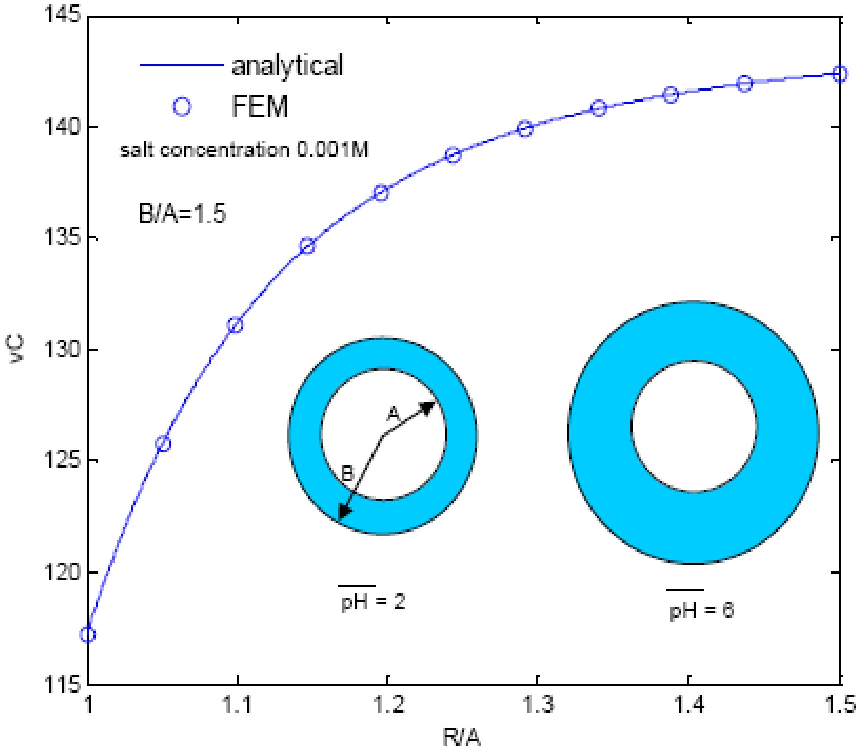
Legendre transformation $\hat{W} = W - (\mu_+ - \mu_{H^+})C_+ - (\mu_- + \mu_{H^+})C_- - \mu_S C_S$

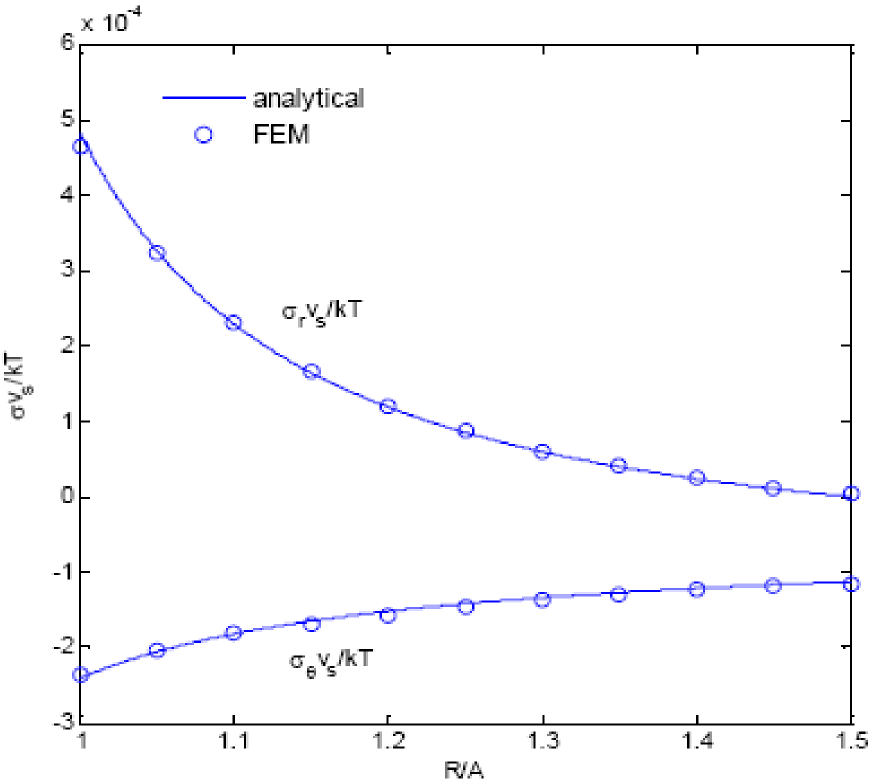
$$\int \delta \hat{W} dV = \int B_i \delta x_i dV + \int T_i \delta x_i dA$$

$$W = W\left(\mathbf{F}, C_+, C_-, C_{H^+}\right) \longrightarrow \begin{cases} c_- / \overline{c}_- = \left(c_{H^+} / \overline{c}_{H^+}\right)^{-1} \\ c_+ / \overline{c}_+ = c_{H^+} / \overline{c}_{H^+} \\ \dfrac{c_{H^+}\left(c_{H^+} + c_+ - c_-\right)}{\left(f / v\right)\left(\det \mathbf{F}\right)^{-1} - \left(c_{H^+} + c_+ - c_-\right)} = N_A K_a \end{cases} \longrightarrow \hat{W} = \hat{W}\left(\mathbf{F}, \overline{c}_{H^+}, \overline{c}_+\right)$$

Marcombe, Cai, Hong, Zhao, Lapusta, Suo, submitted

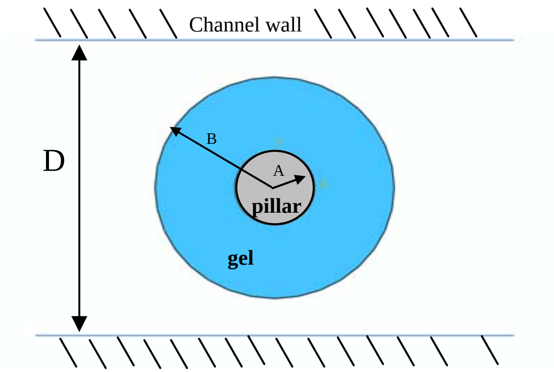
Core-shell structure



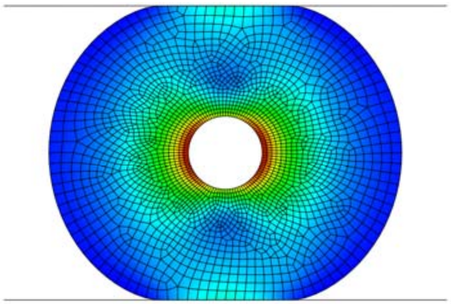


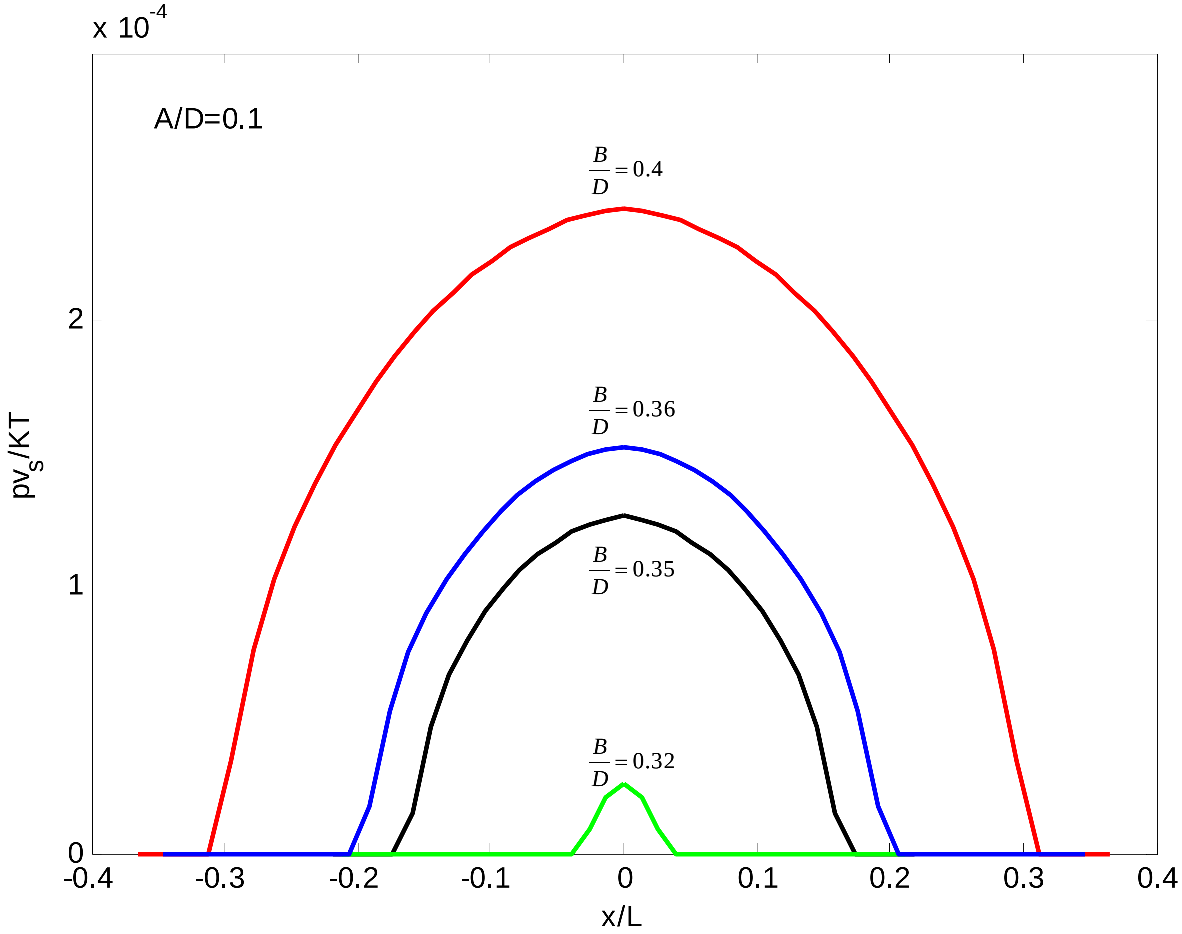
FEM results

pH = 2



pH = 6





Soft Active Materials (SAM)

Soft: large deformation in response to small forces
(e.g., rubbers, gels)

Active: large deformation in response to diverse stimuli
(e.g., electric field, temperature, pH, salt)

Stimuli cause deformation.

Deformation does something useful.

Summary

- Convergence of two worlds (soft biology, hard engineering).
- Soft active materials (SAMs) have many uses (soft robots, adaptive optics, self-regulating fluidics, oil recovery, energy harvesting, drug delivery, tissue regeneration, low-cost diagnosis...).
- Science of SAMs is interesting and challenging (mechanics, electricity, and chemistry).
- The field is wide open (fabrication, computation, imagination).