Large deformation and electrochemistry of polyelectrolyte gels

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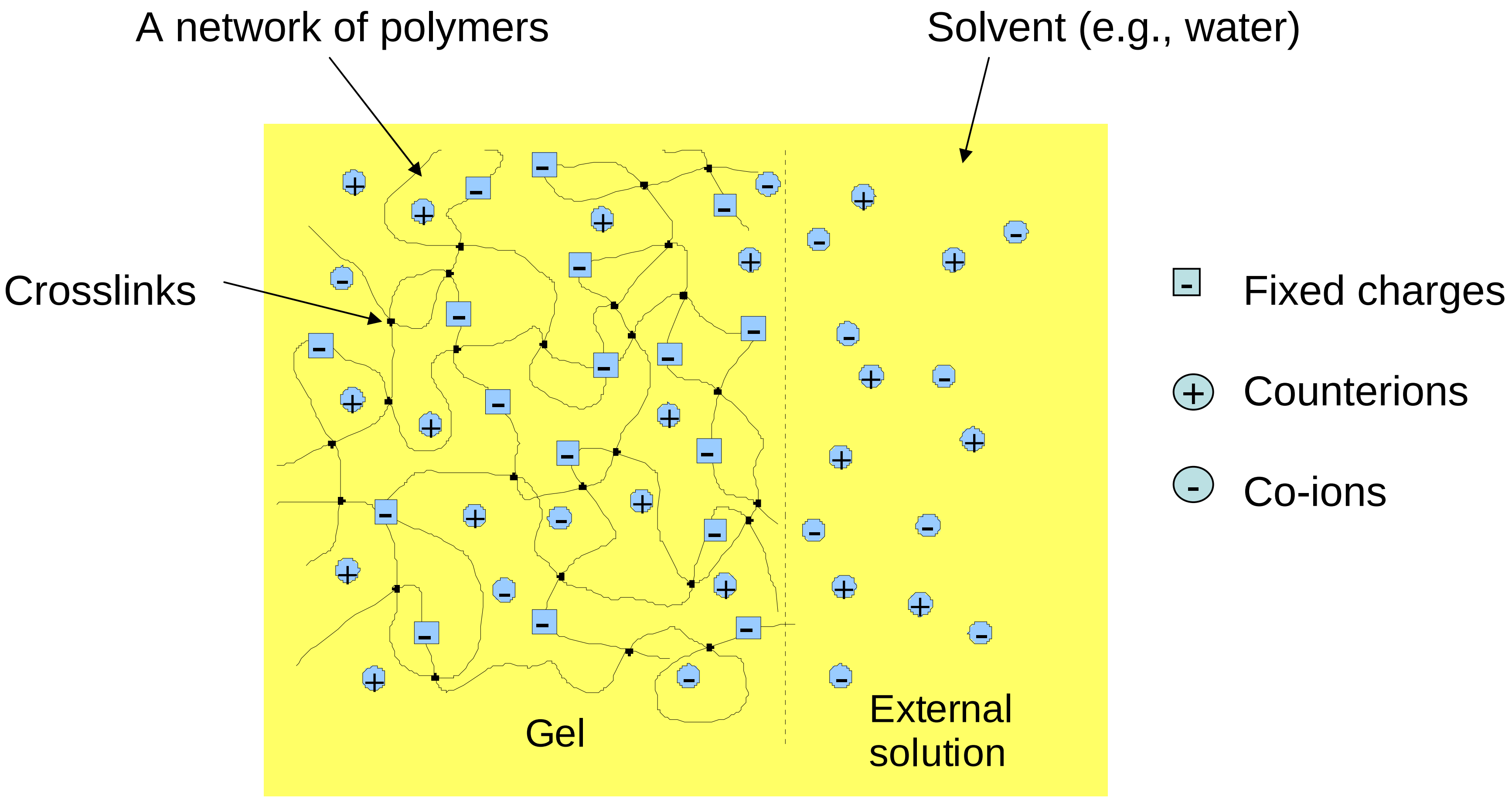
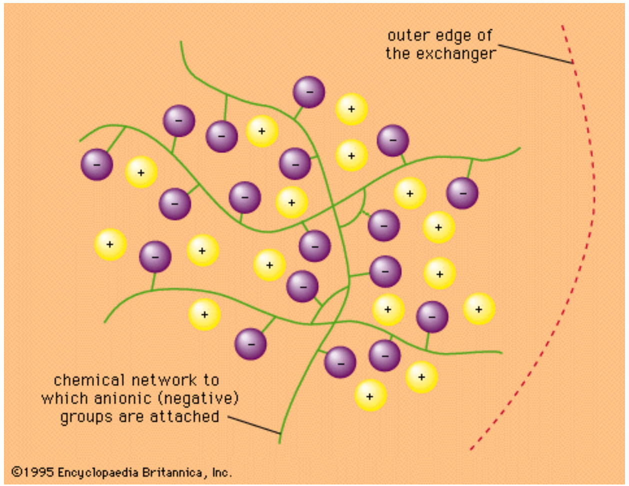
Polyelectrolyte gels

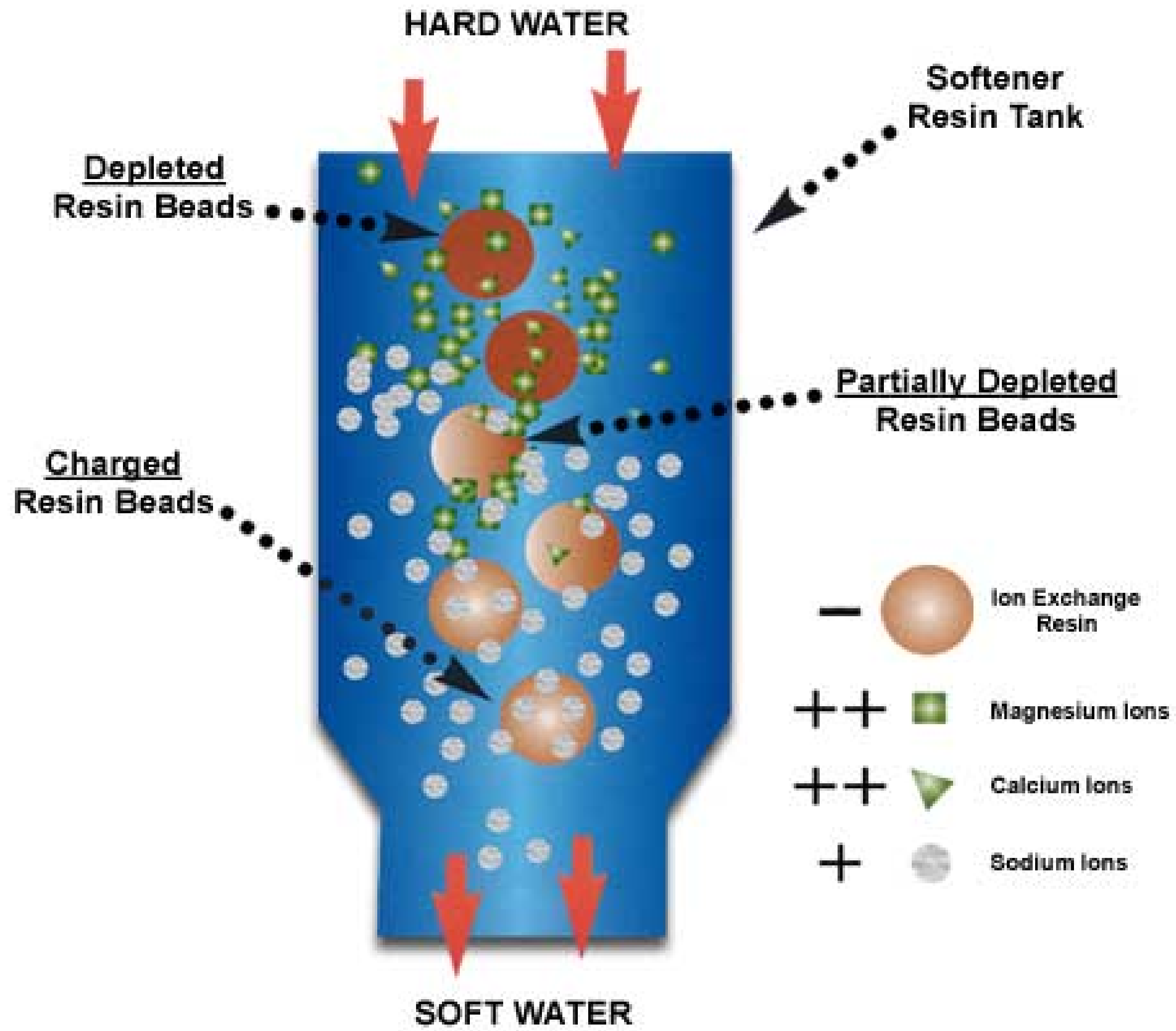


Most tissues of animals and plants are polyelectrolyte gels.

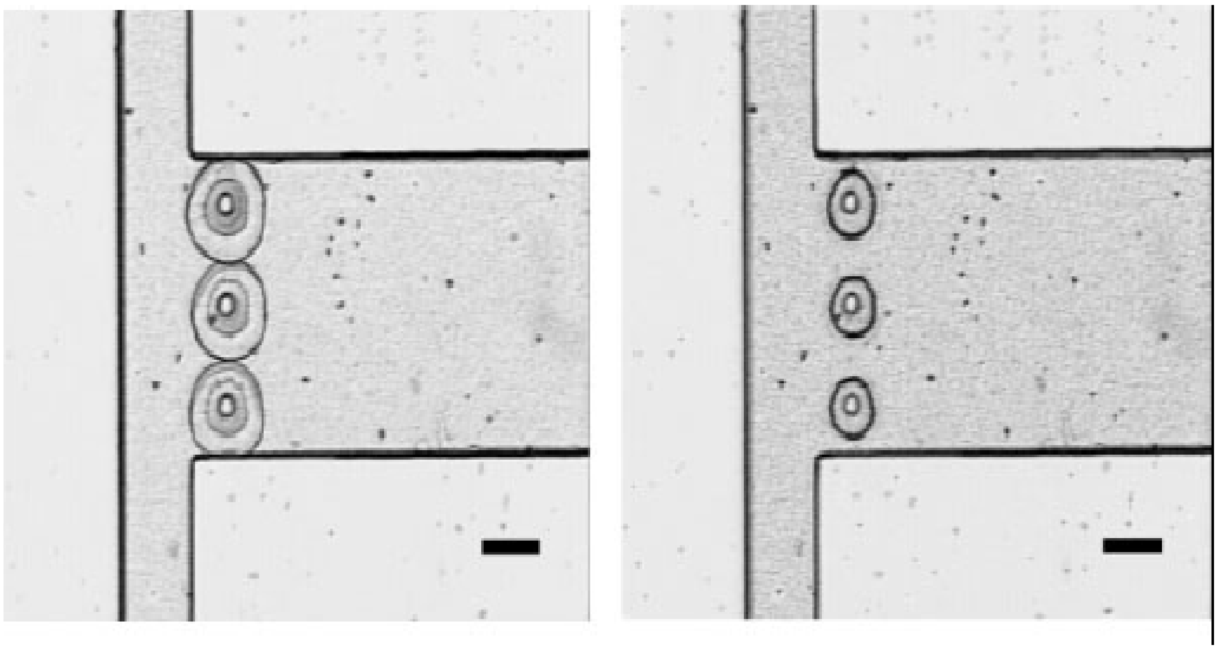
Ion exchanger

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





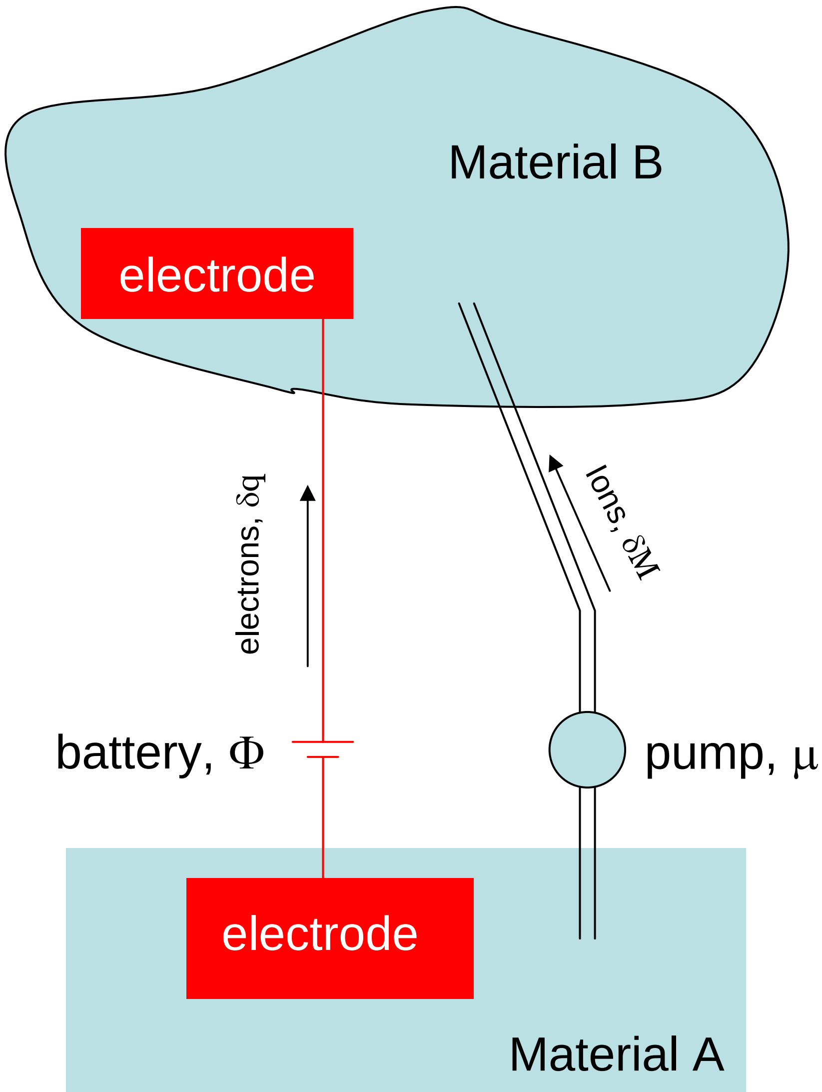
pH-sensitive valves in microfluidics



Deformation and force regulated by physiological variables (pH, salt, temperature…)
Mechanics and chemistry

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

Electric potential
Electrochemical potential



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

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

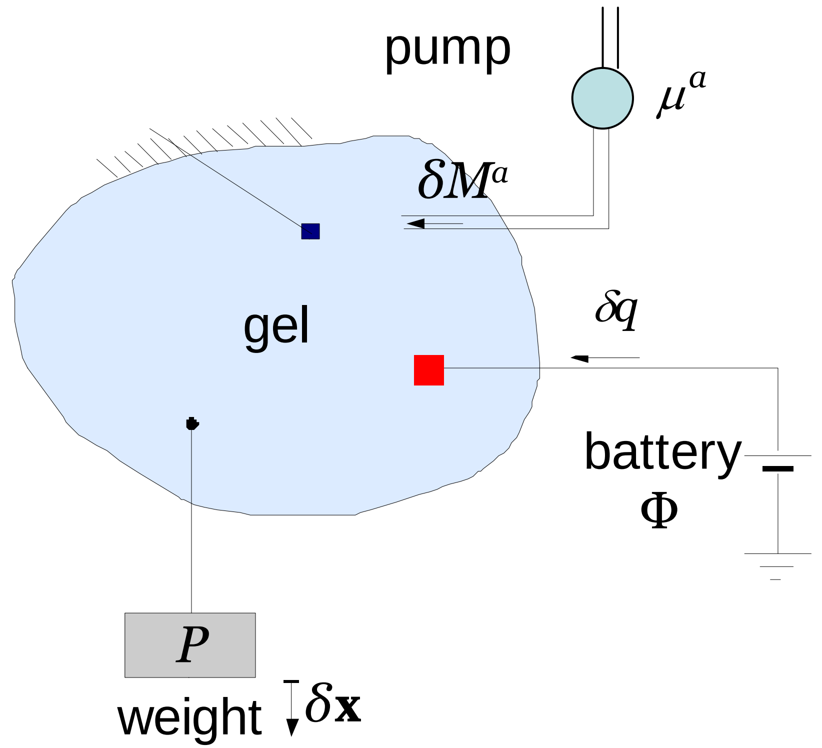
neutrality $$\delta q + ez\delta M = 0$$

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

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

Gibbs (1878)

3 ways of doing work to a gel



$$\int \delta W dV = \int B_i \delta x_i dV + \int T_i \delta x_i dA + \int \Phi\, \delta q dV + \int \Phi\, \delta \omega dA + \sum_a \mu^a \int \delta C^a dV$$

$$W = \frac{\text{free energy of gel}}{\text{volume in reference state}} \qquad C^a(\mathbf{X},t) = \frac{\#\text{of ions of species } a}{\text{volume in reference state}}$$

A field theory of thermodynamic equilibrium

Deformation gradient

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

Gauss's law

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

Concentrations

$$C^a(\mathbf{X},t)$$

$$Q=q+\sum ez^aC^a+ez^{fix}C^{fix}$$

Material model:

$$W=W\left(\mathbf{F},\tilde{\mathbf{D}},C^1,C^2,\cdots\right)$$

Equilibrium:

$$\int \delta W dV=\int B_i\delta x_i dV+\int T_i\delta x_i dA+\int \Phi\,\delta q dV+\int \Phi\,\delta\omega dA+\sum_a \mu^a\int \delta C^a dV$$

Equivalent conditions of equilibrium

$$s_{iK}=\frac{\partial W}{\partial F_{iK}}$$

$$\tilde{E}_K=\frac{\partial W}{\partial \tilde{D}_K}$$

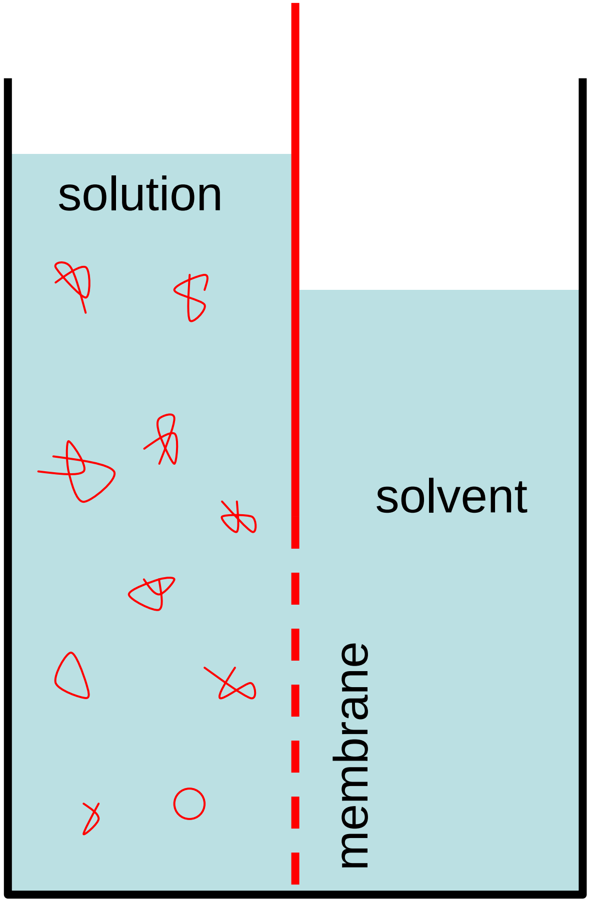
$$\mu^a=ez^a\Phi+\frac{\partial W}{\partial C^a}$$

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

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

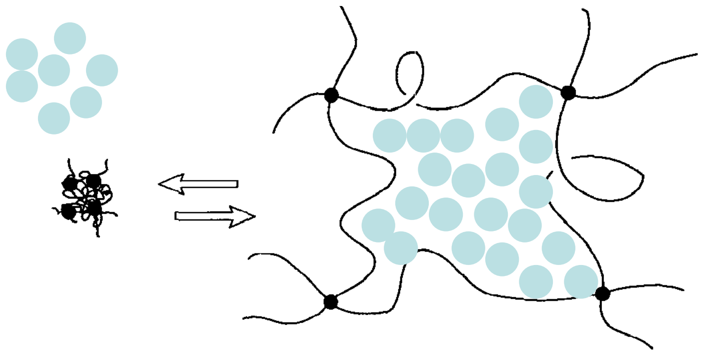
$$\mu^a=\text{constant}$$

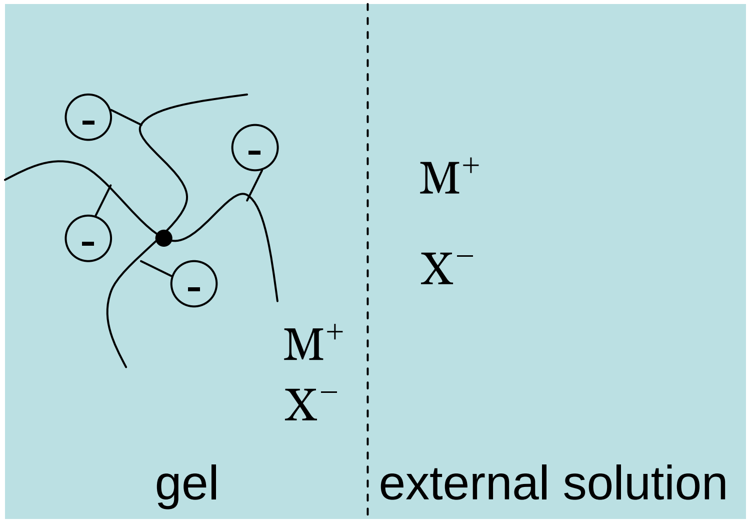
Osmosis



$$\Pi = \frac{N}{V} kT$$

microscopic processes





- Swelling increases entropy by mixing solvent and polymers.
- Swelling decreases entropy by straightening the polymers.
- Redistributing mobile ions increases entropy by mixing.
- Neutrality reduces electrostatic energy.

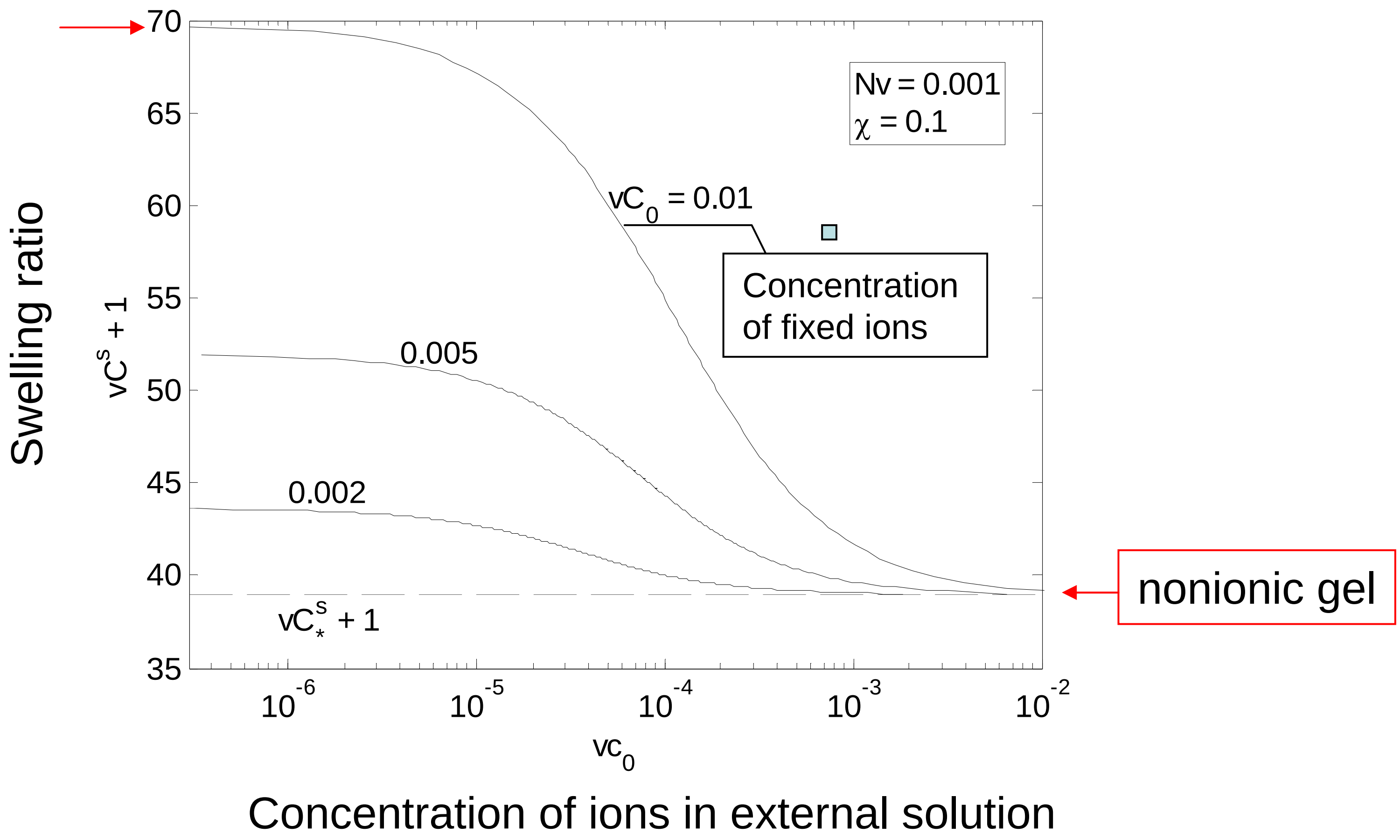
Free-energy function

Free-energy function $W\left(\mathbf{F}, C^a, \tilde{\mathbf{D}}\right) = W_s(\mathbf{F}) + W_m\left(C^1, C^2, \cdots\right) + W_p\left(\mathbf{F}, \tilde{\mathbf{D}}\right)$

- Free energy of stretching $W_s(\mathbf{F}) = \frac{1}{2} NkT\left[F_{iK}F_{iK} - 3 - 2\log(\det \mathbf{F})\right]$
- Free energy of mixing $W_m\left(C^a\right) = kT\left(C^s \log\frac{vC^s}{1+vC^s} - \frac{\chi/v}{1+vC^s}\right) + kT\sum_{b\neq s} C^b\left(\log\frac{C^b}{vC^s c_0^b} - 1\right)$
- Free energy of polarization $W_p\left(\mathbf{F}, \tilde{\mathbf{D}}\right) = \frac{1}{2\varepsilon}\frac{F_{iK}F_{iL}}{\det \mathbf{F}}\tilde{D}_K \tilde{D}_L$

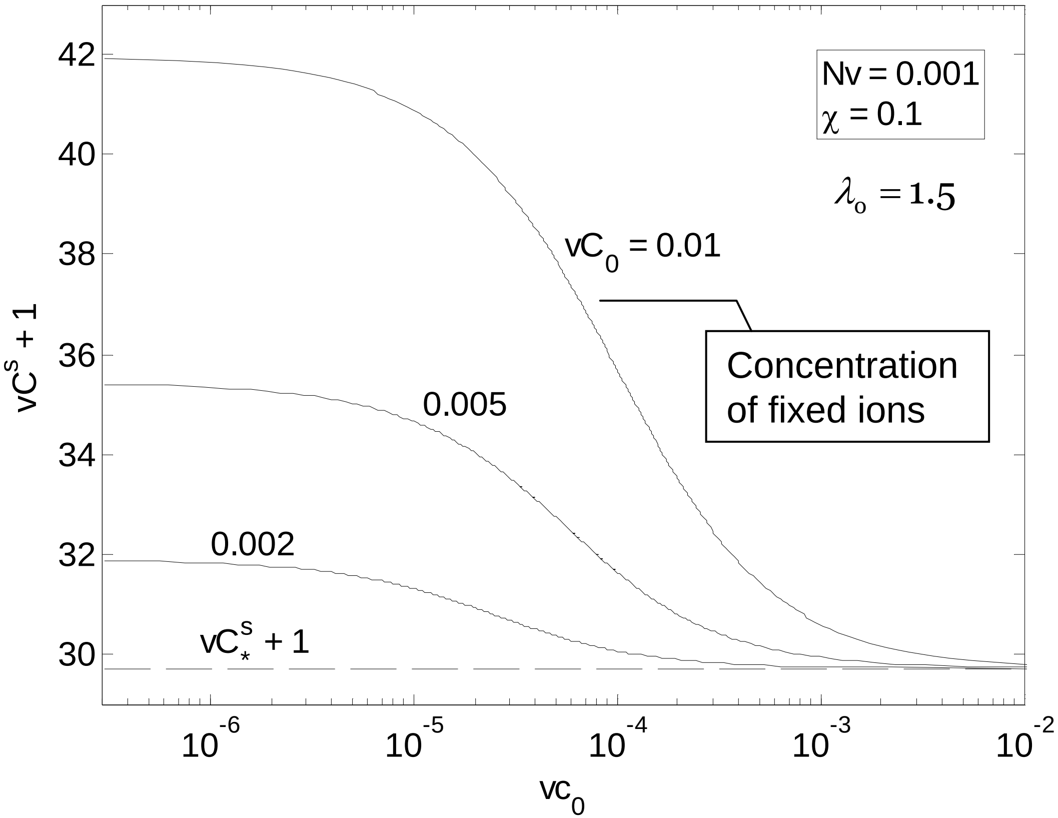
Flory, Rehner, J. Chem. Phys., 11, 521 (1943) Zhao, Hong, Suo, Physical Review B 76, 134113 (2007)

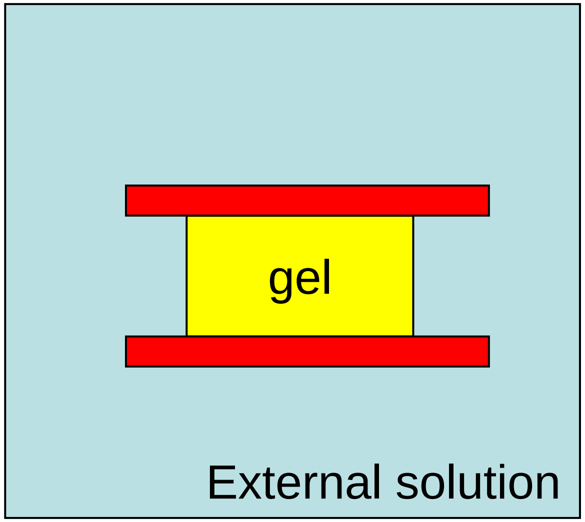
Swelling regulated by concentration of ions



Constrained swelling

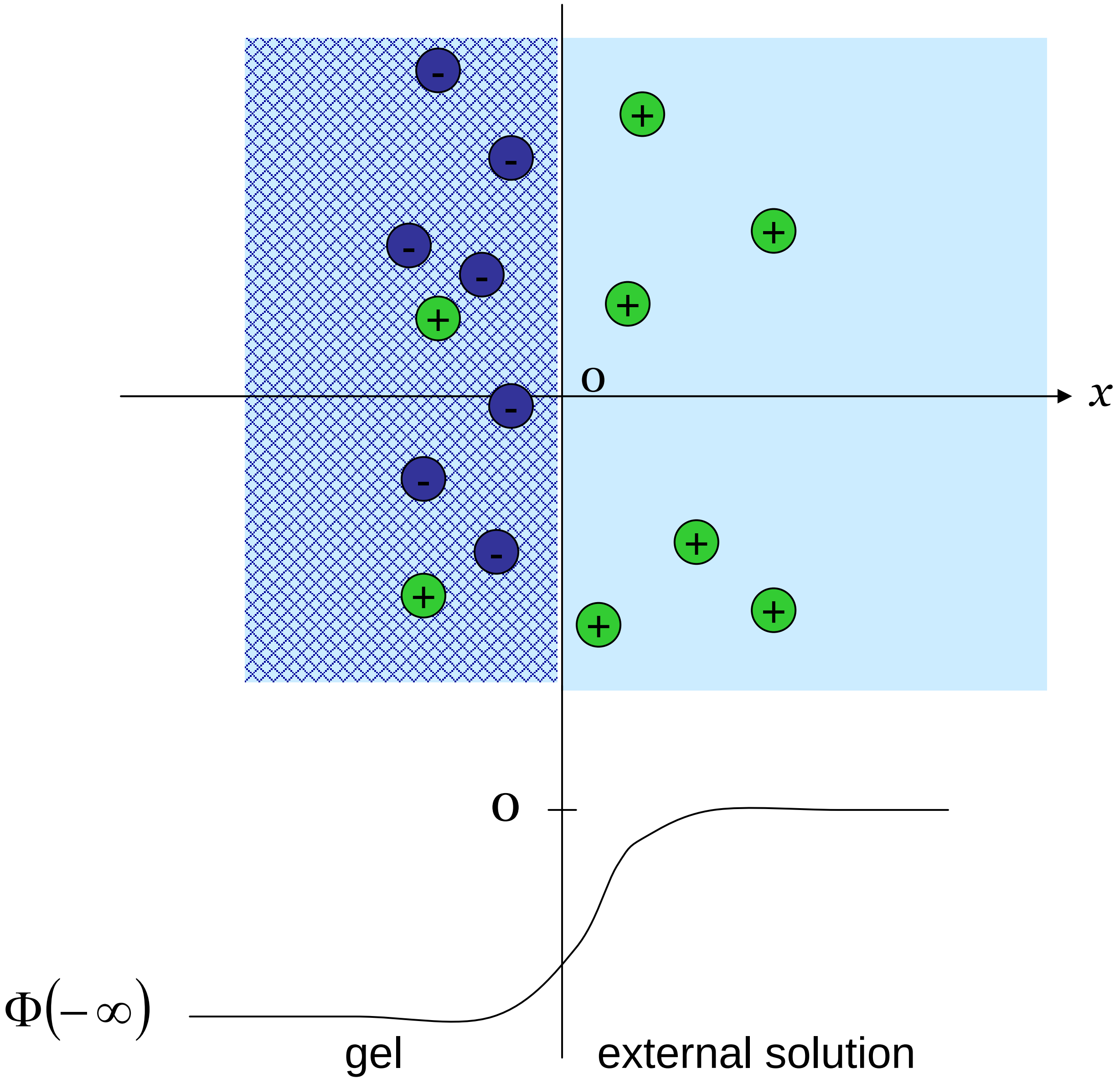
Swelling ratio





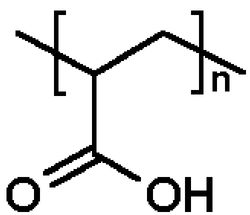
Concentration of ions in external solution

Debye length



$$L_D = \sqrt{\frac{kT\varepsilon}{2e^2 c_0}}$$

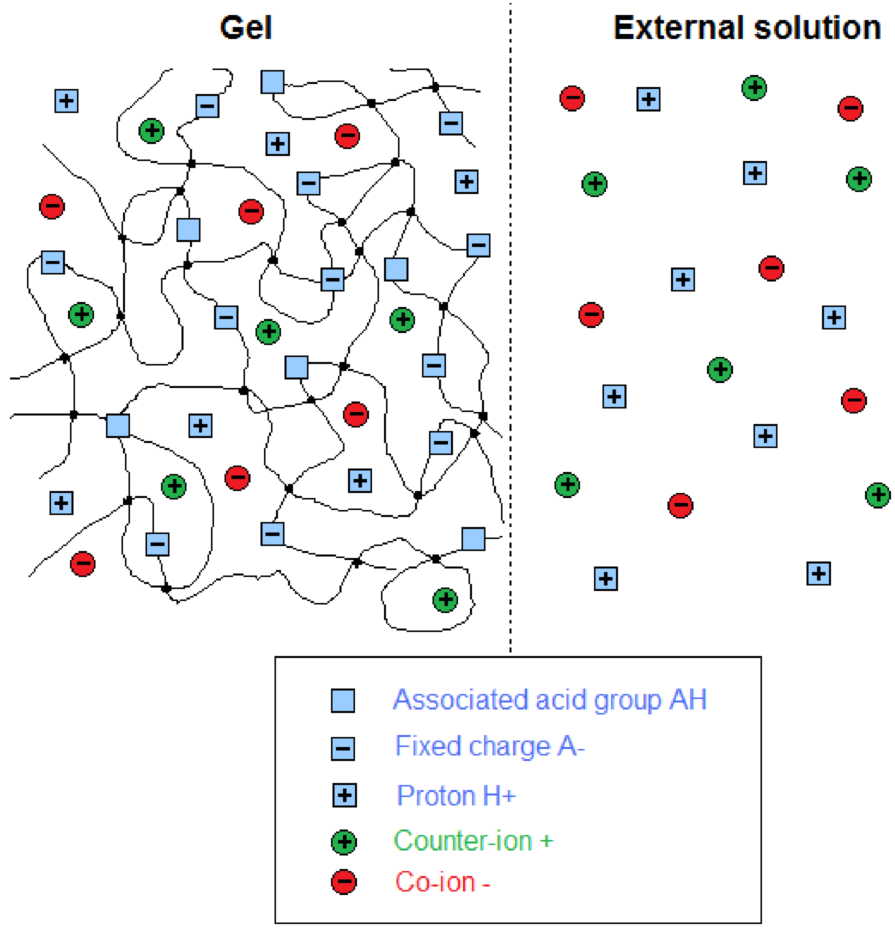
pH-sensitive gel



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

fixed mobile

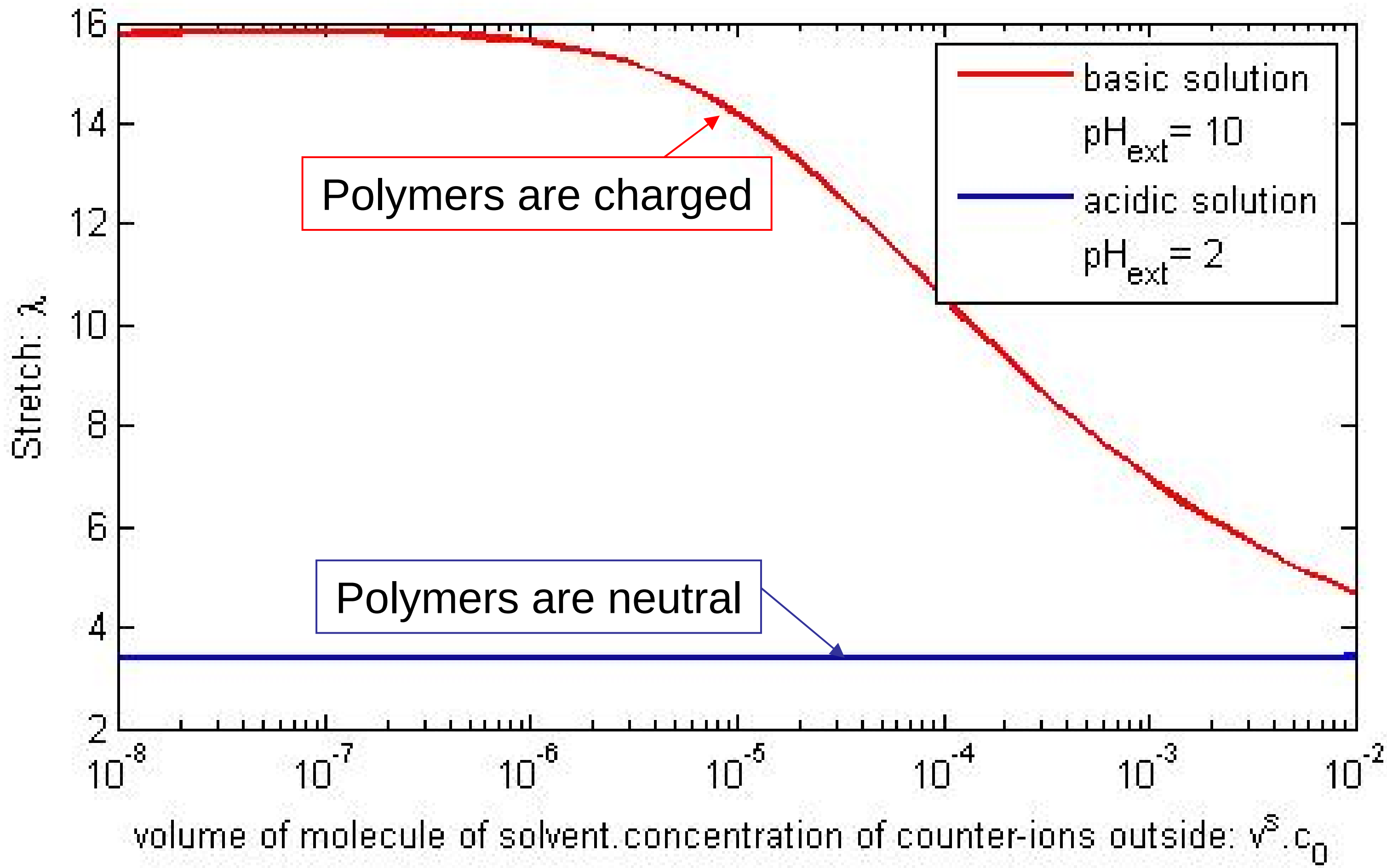
$$\frac{[\mathrm{RCOO^-}][\mathrm{H^+}]}{[\mathrm{RCOOH}]} = K$$



pH-sensitive gel - Free Swelling - influence of pH_{ext}

Dimensionless concentration of polymer chains: $N.v^S = 0.001$
Molar fraction of acidic group in polymer: f= 25 %
Flory's interaction parameter: $\chi = 0.1$

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



Summary

- Couple large deformation and electrochemistry.
- Swelling regulated by concentration of ions.
- Swelling regulated by pH.