Mechanics and electrochemistry of polyelectrolyte gels

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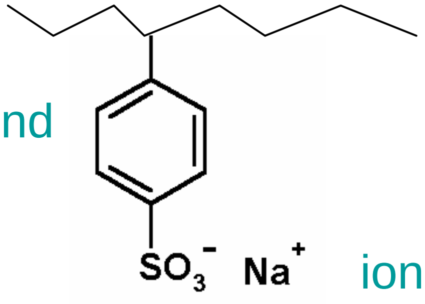
Work with **W. Hong** and **X. Zhao**

Polyelectrolyte: polymer with electrolyte group

http://en.wikipedia.org/wiki/Polyelectrolyte

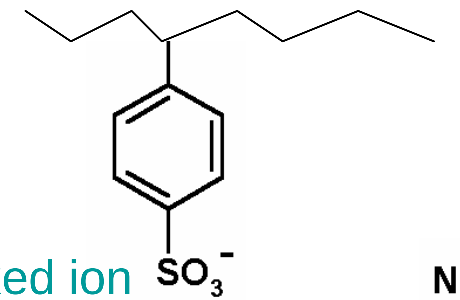
covalent bond



ionic bond

In a solvent, the electrolyte dissociates.

solvent



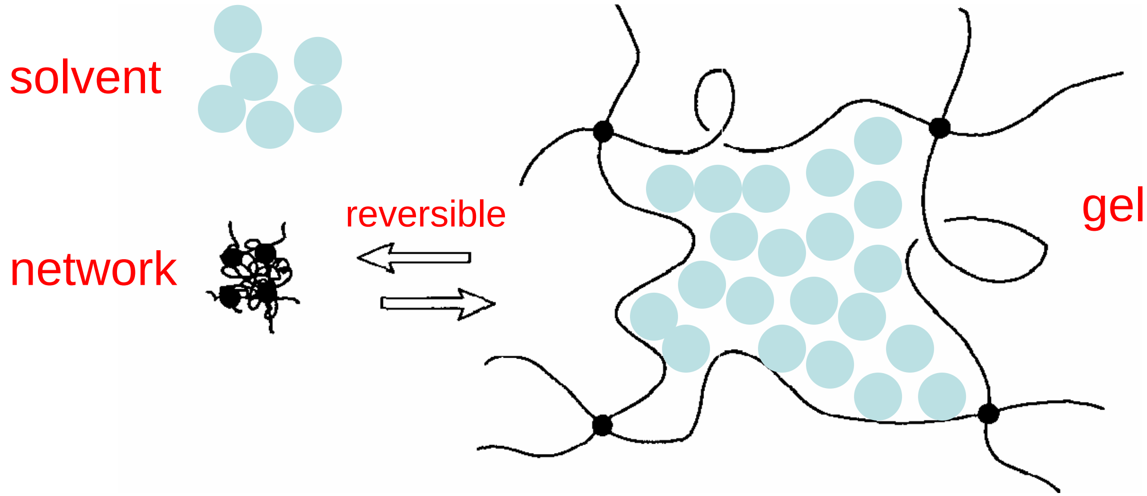
Cl^-
co-ion

fixed ion

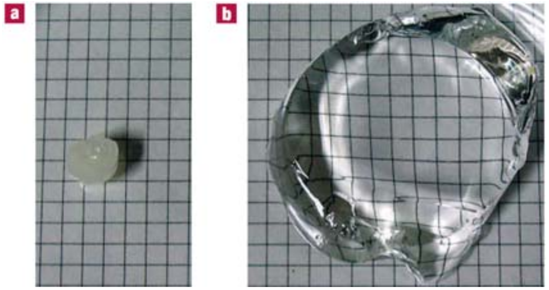
Na^+
counterion

Ca^{++}
counterion

gel = network + solvent

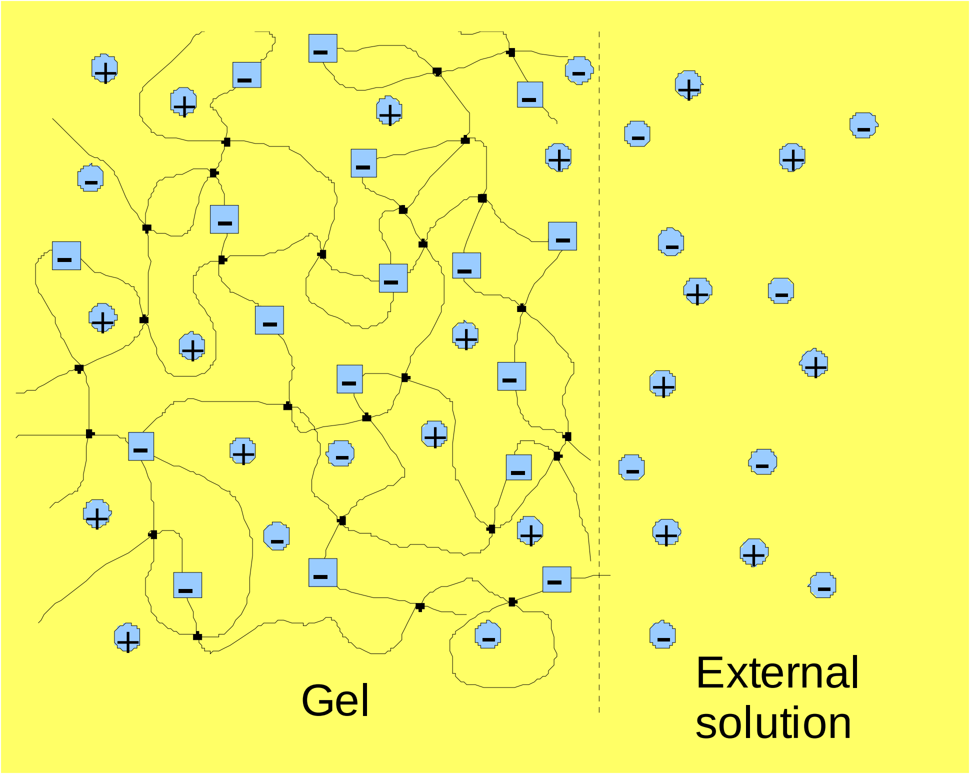


Solid-like: long polymers crosslink by strong bonds. Retain shape
Liquid like: polymers and solvent aggregate by weak bonds. Enable transport



Ono, Sugimoto, Shinkai, Sada, Nature Materials 6, 429, 2007

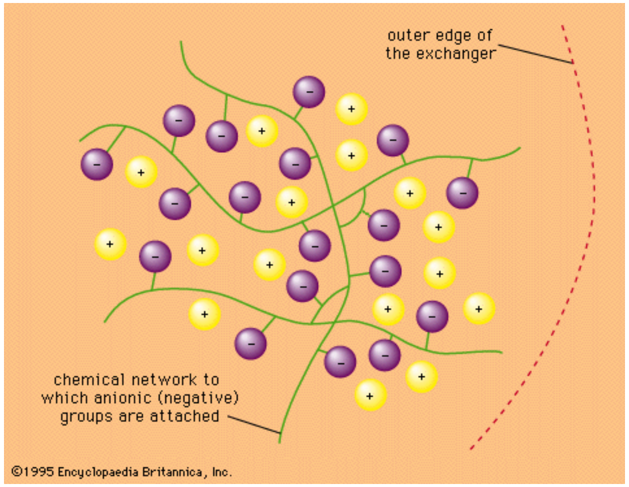
Polyelectrolyte gels

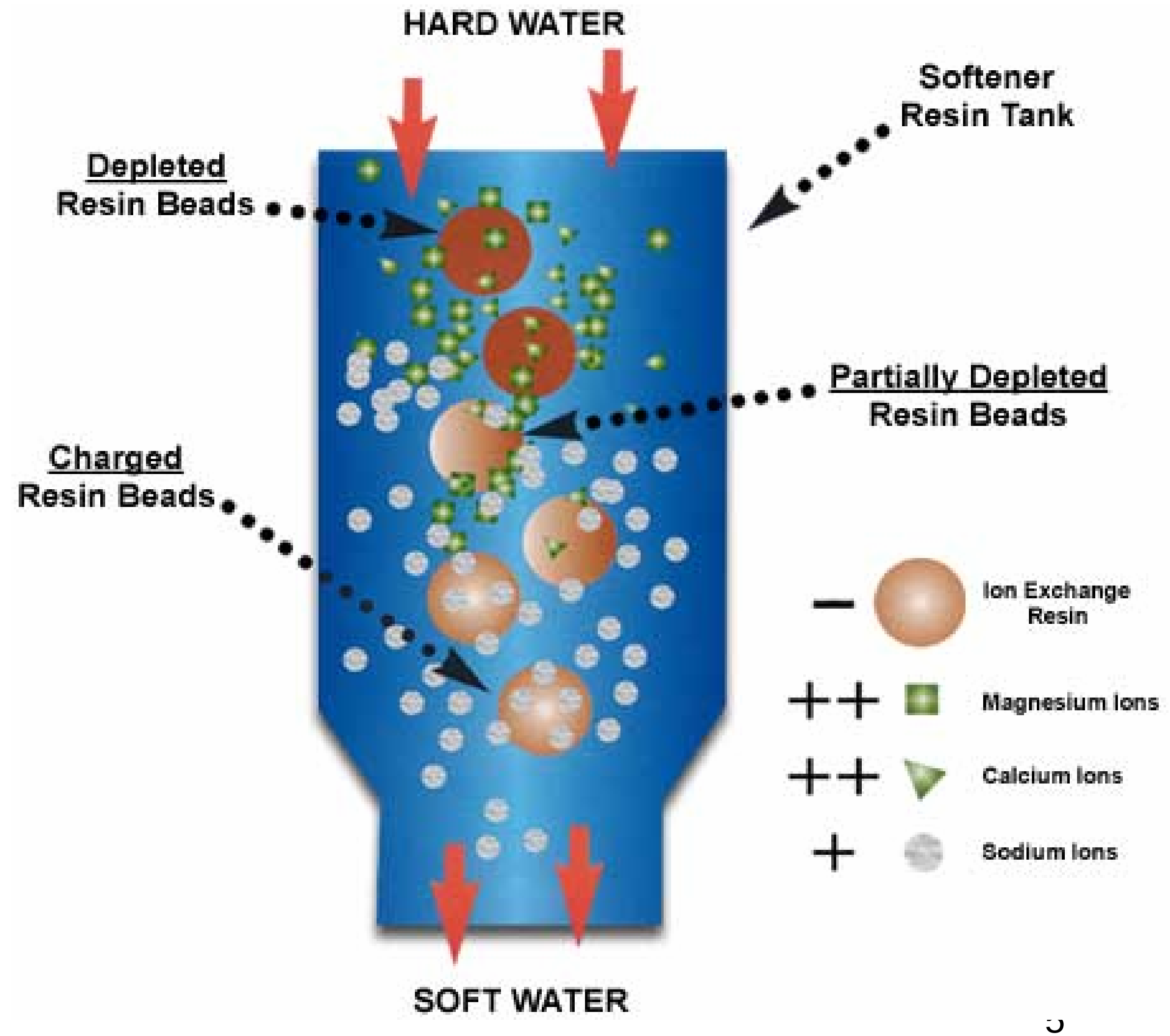


- •Network
- •Solvent
- •Fixed ions
- •Mobile ions

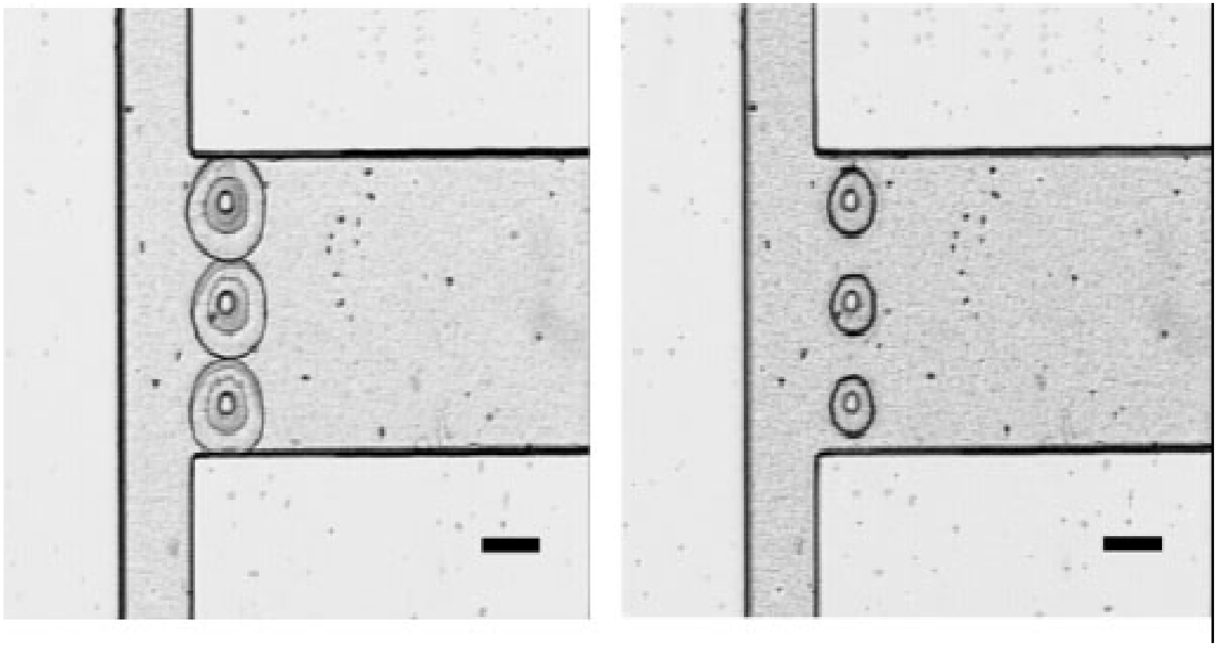
Ion exchange resin

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



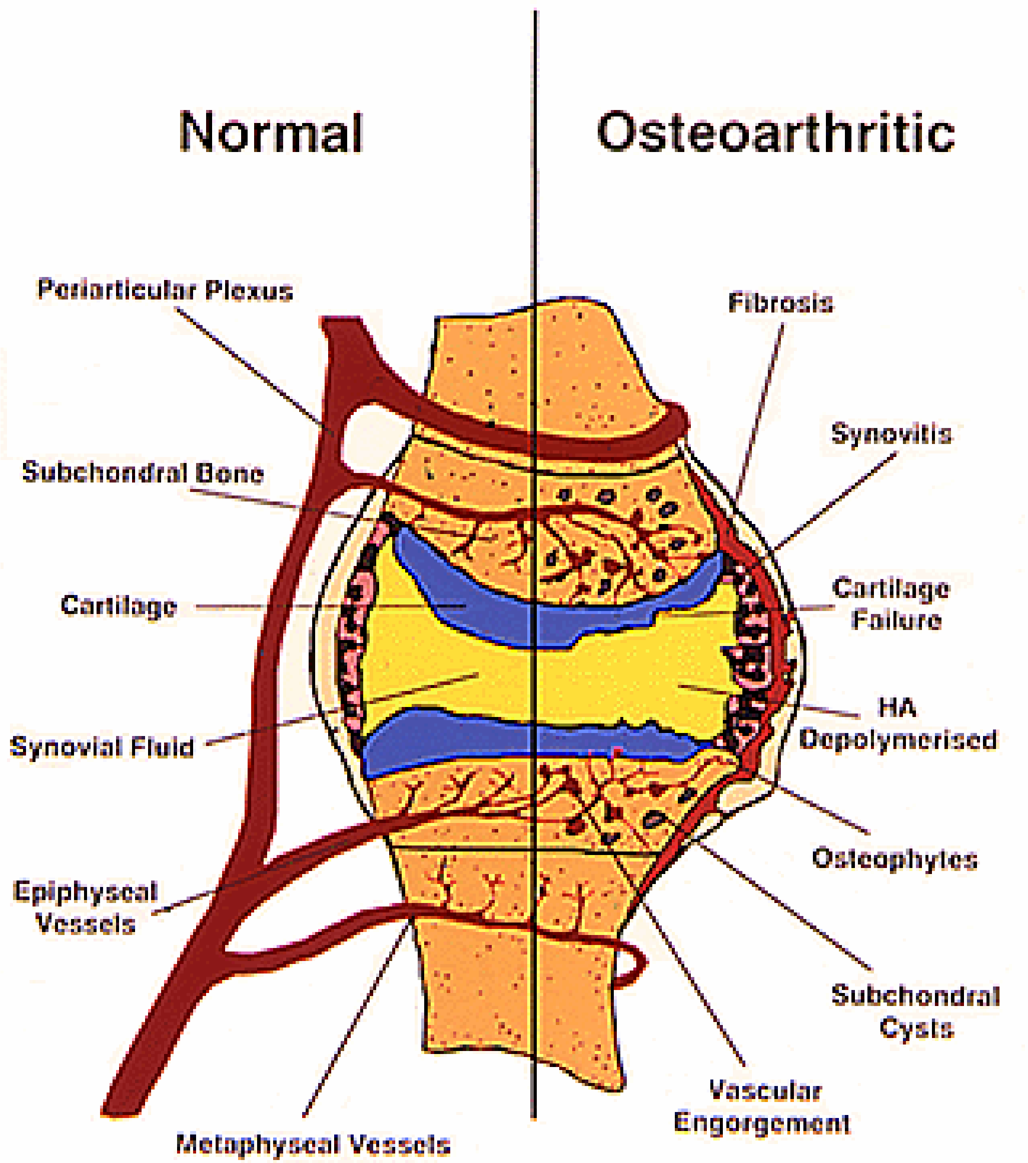


pH-sensitive valves in microfluidics



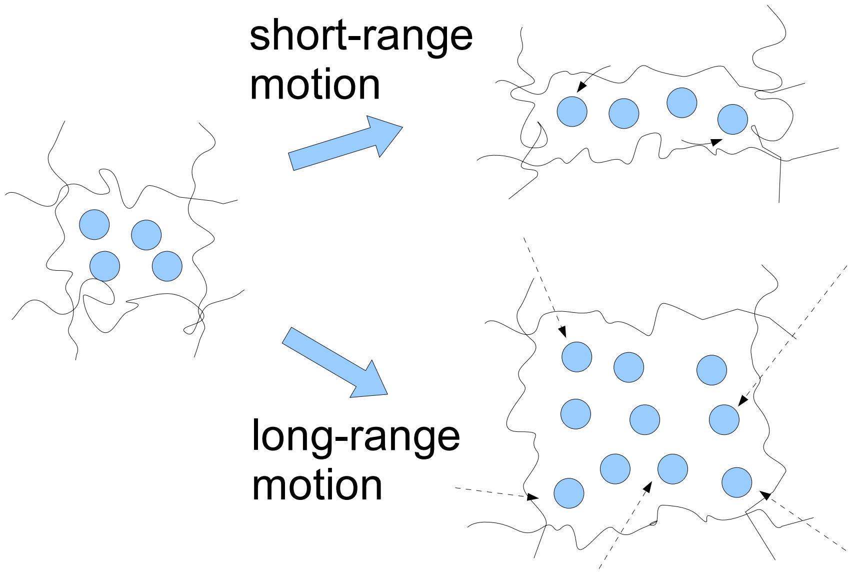
Beebe, Moore, Bauer, Yu, Liu, Devadoss, Jo, Nature 404, 588 (2000)

Many tissues are polyelectrolyte gels



Structure and function:
- Cartilage is polyelectrolyte.
- Does this fact have anything to do with low friction of a joint?

Time-dependent process

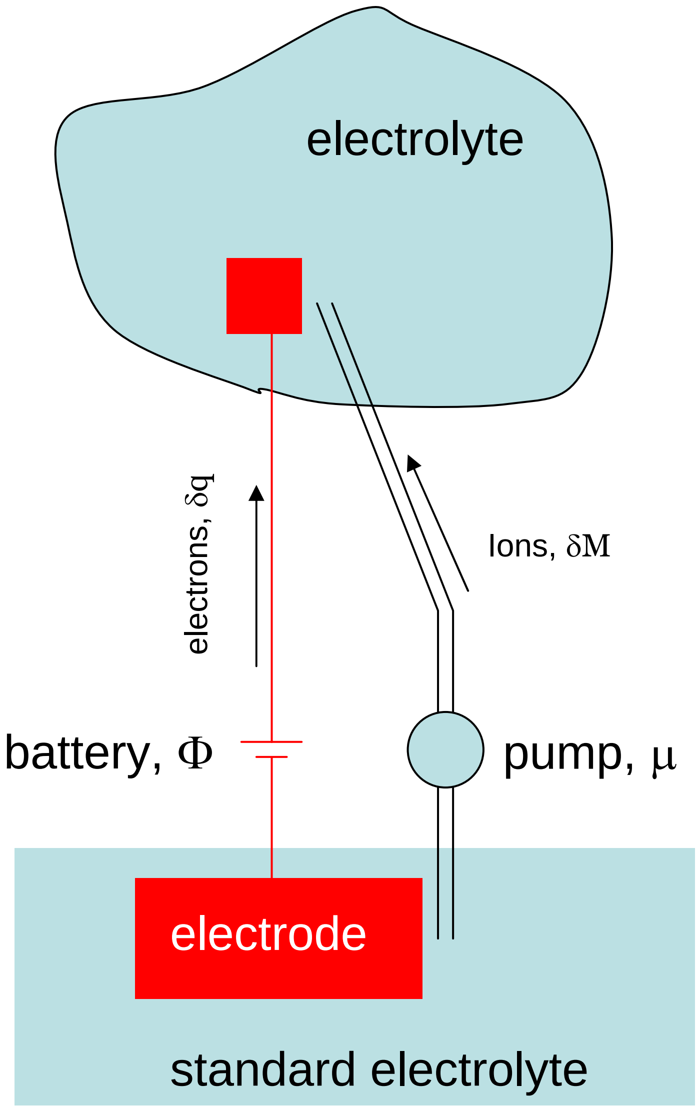


Shape change: short-range motion of solvent molecules, fast
Volume change: long-range motion of solvent molecules, slow

Hong, Zhao, Zhou, Suo, JMPS 56, 1779 (2008)

Electrochemical potential

Work done to pump an ion from one electrolyte to another



- work done by the battery, $\Phi \delta q$
- work done by the pump, $\mu \delta M$
- Helmholtz free energy, F

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

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

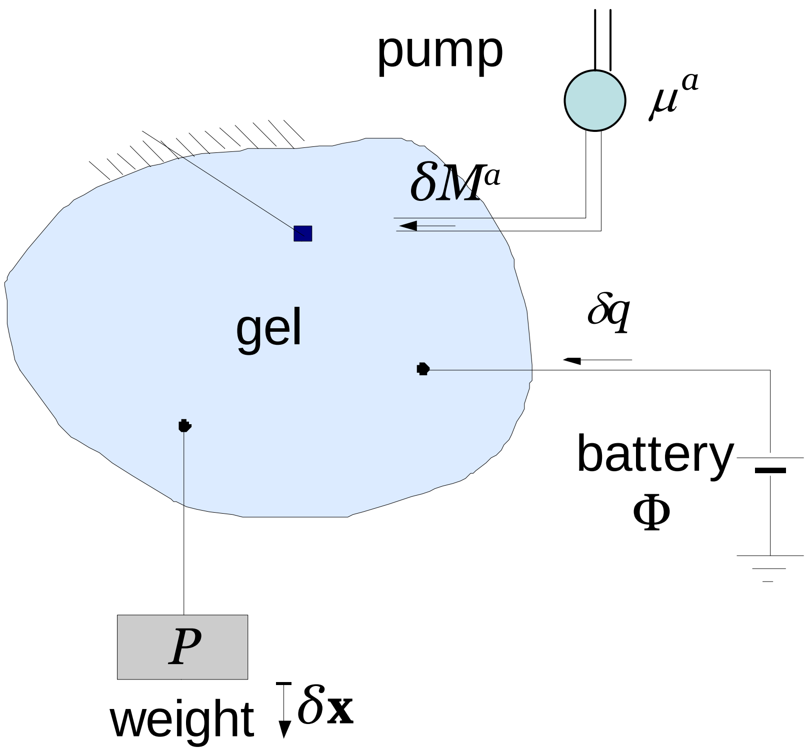
$$\delta F = (-ez\Phi + \mu)\delta M$$

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

Gibbs (1878)

3D inhomogeneous state of equilibrium

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



$$W = \frac{\text{free energy of gel}}{\text{volume in reference state}}$$

$$C^a(\mathbf{x},t) = \frac{\#\text{of ions of species } a}{\text{volume in reference state}}$$

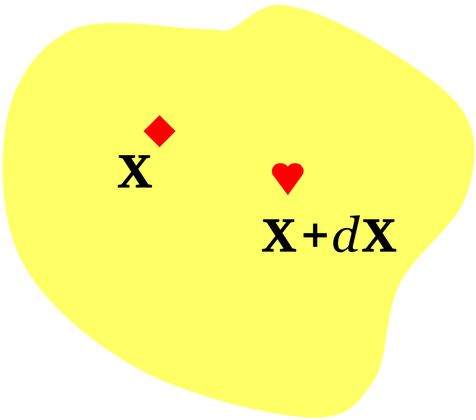
3 ways of doing work to a gel

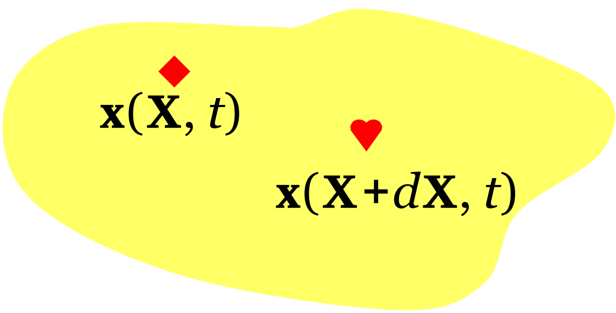
A field of markers: stretch

Reference state

Current state

$$\lambda = \frac{l}{L}$$

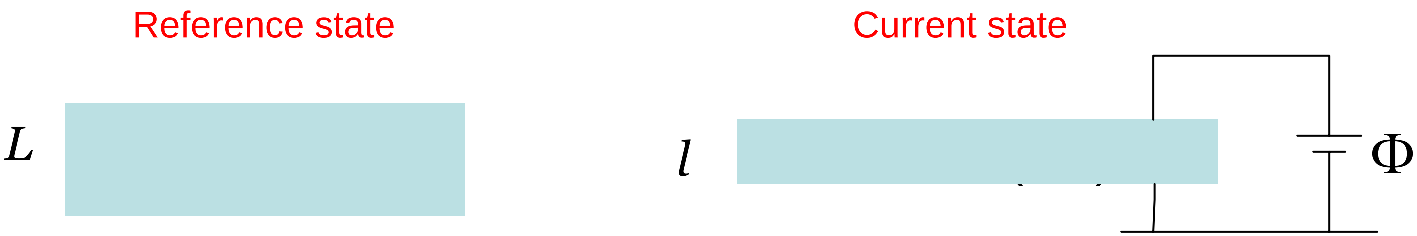




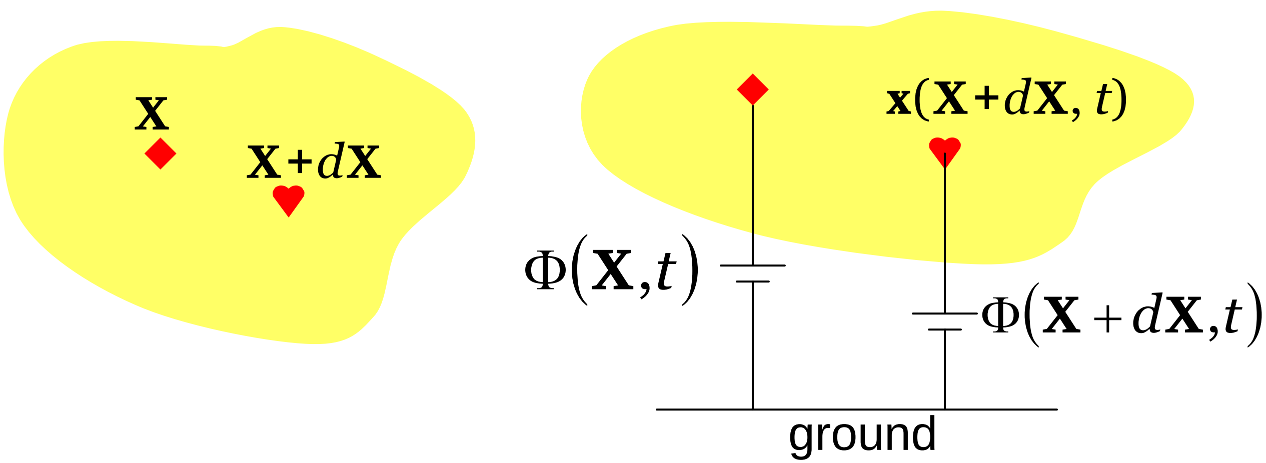
$$\frac{x_i(\mathbf{X}+d\mathbf{X},t)-x_i(\mathbf{X},t)}{dX_K}$$

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

A field of batteries: electric field



$$\tilde{E} = \frac{\Phi}{L}$$

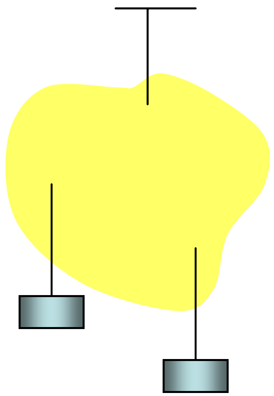


$$\frac{\Phi(\mathbf{X}+d\mathbf{X},t)-\Phi(\mathbf{X},t)}{dX_K}$$

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

A field of weights: stress

Define the stress s_{iK}, such that



$$\int s_{iK} \frac{\partial \xi_i}{\partial X_K} dV = \int B_i \xi_i dV + \int T_i \xi_i dA$$

holds for any test function $\xi_i(\mathbf{X})$

Apply divergence theorem, one obtains that

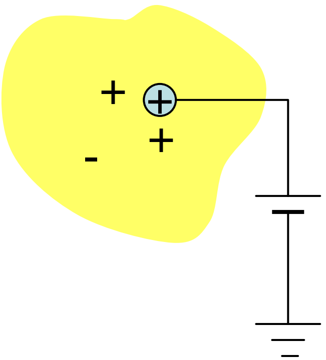
$$\frac{\partial s_{iK}(\mathbf{X},t)}{\partial X_K} + B_i(\mathbf{X},t) = 0 \qquad \left(s_{iK}^{-}(\mathbf{X},t) - s_{iK}^{+}(\mathbf{X},t)\right) N_K(\mathbf{X},t) = T_i(\mathbf{X},t)$$

in volume

on interface

A field of charges: electric displacement

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



Define the electric displacement $\tilde{D}_K$, such that

$$-\int \frac{\partial \zeta}{\partial X_K} \tilde{D}_K dV = \int \zeta Q dV + \int \zeta \omega dA$$

holds for any test function $\zeta(\mathbf{X})$.

Apply divergence theorem, one obtains that

$$\frac{\partial \tilde{D}_K(\mathbf{X},t)}{\partial X_K} = Q(\mathbf{X},t) \qquad \left(\tilde{D}_K^+(\mathbf{X},t) - \tilde{D}_K^-(\mathbf{X},t)\right) N_K(\mathbf{X},t) = \omega(\mathbf{X},t)$$

in volume

on interface

Equilibrium conditions

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

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

$$\Downarrow$$

$$\boxed{s_{iK} = \frac{\partial W}{\partial F_{iK}}} \qquad \boxed{\tilde{E}_K = \frac{\partial W}{\partial \tilde{D}_K}} \qquad \boxed{\mu^a = ez^a \Phi + \frac{\partial W}{\partial C^a}}$$

Sum up: a field theory

A field of markers

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

A field of batteries

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

A field of weights

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

A field of charges

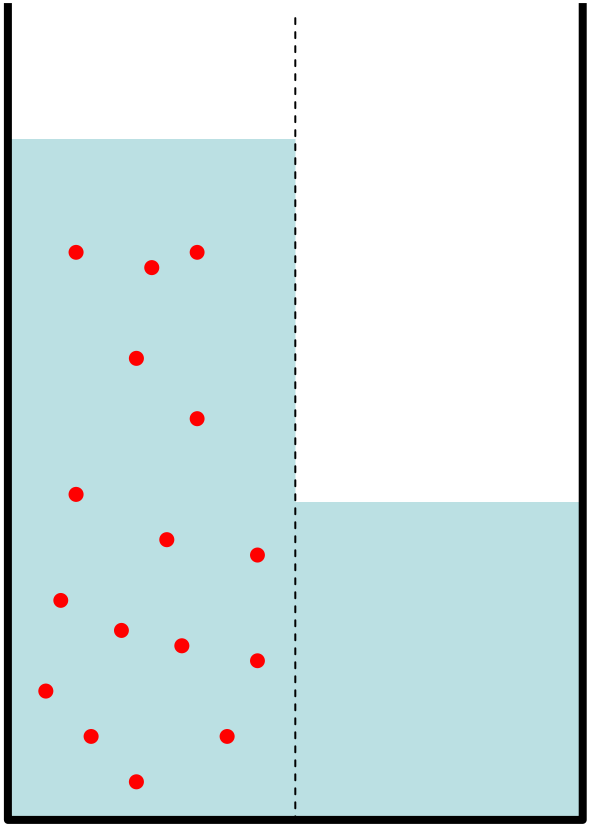
$$\frac{\partial\tilde{D}_K(\mathbf{X},t)}{\partial X_K}=Q(\mathbf{X},t)$$

$$C^a(\mathbf{X},t) \qquad Q=q+\sum ez^aC^a+ez^{fix}C^{fix}$$

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

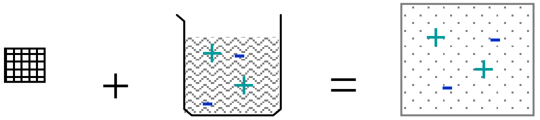
$$s_{iK}=\frac{\partial W}{\partial F_{iK}} \qquad \tilde{E}_K=\frac{\partial W}{\partial\tilde{D}_K} \qquad \mu^a=ez^a\Phi+\frac{\partial W}{\partial C^a}$$

Osmosis



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

Incompressibility of particles



$$V_{\mathrm{dry}} + V_{\mathrm{sol}} = V_{\mathrm{gel}}$$

$$1+\sum_a v^a C^a = \det \mathbf{F}$$

v^a – volume per particle of species a

Assumptions:

- Individual solvent molecule and polymer are incompressible.
- Gel has no voids. (a gel is different from a sponge.)
- An ion occupies a same volume in the solvent and in the gel

Osmotic pressure

Enforce incompressibility as a constraint by introducing a Lagrange multiplier Π

$$\hat{W} = W\left(\mathbf{F}, C^a, \tilde{D}\right) + \Pi\left(1 + \sum v^a C^a - \det \mathbf{F}\right)$$

$$s_{iK} = \frac{\partial W}{\partial F_{iK}} - \Pi H_{iK} \det \mathbf{F}$$

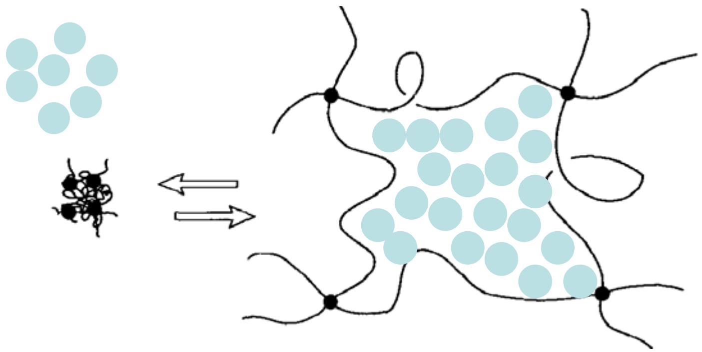
$$\mu^s = \frac{\partial W}{\partial C^s} + \Pi v^s$$ solvent

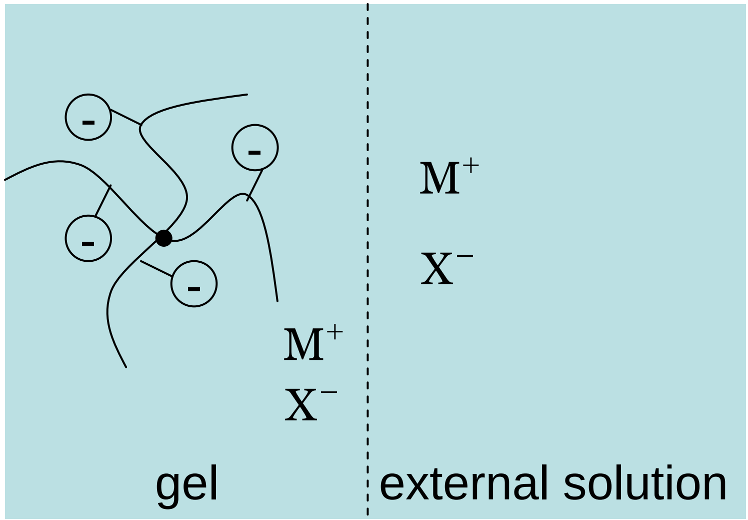
$$\mu^b = \frac{\partial W}{\partial C^b} + e\Phi z^b + \cancel{\Pi v^b}$$ ions

negligible

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

microscopic processes





- Swelling increases entropy by mixing solvent and polymers.
- Swelling decreases entropy by straightening the polymers.
- Redistributing mobile ions increases entropy by mixing.
- Unbalanced changed causes 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 $W_m\left(C^a\right) = kT\left(C^s \log \frac{\upsilon C^s}{1+\upsilon C^s} - \frac{\chi/\upsilon}{1+\upsilon C^s}\right) + kT\sum_{b \neq s} C^b \left(\log \frac{C^b}{\upsilon C^s c_0^b} - 1\right)$
- 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)

Equations of state

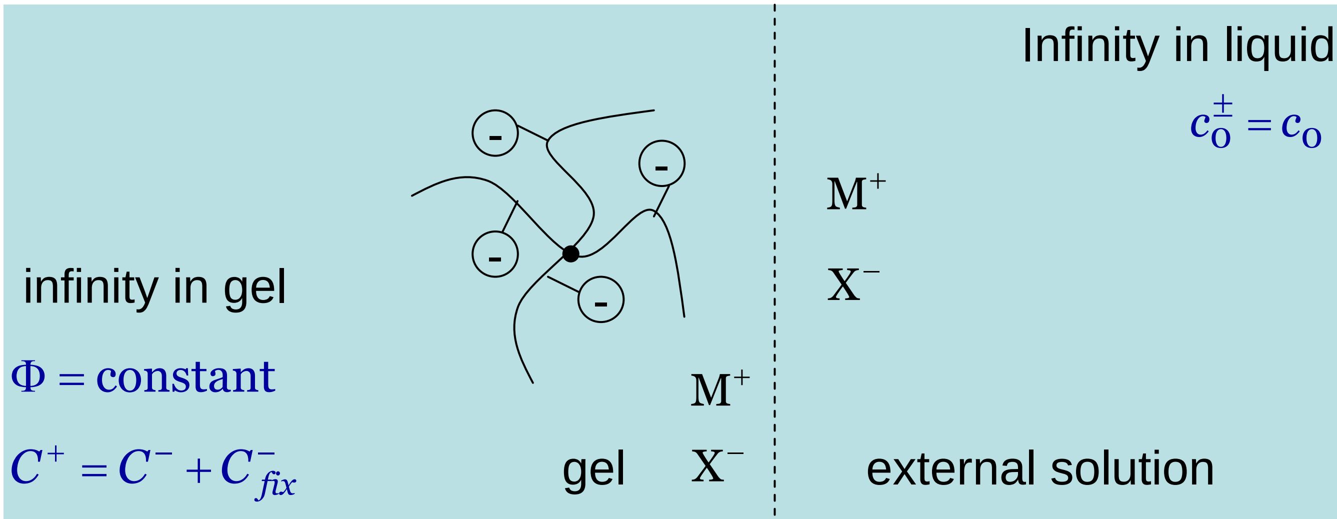
$$s_{iK} = \frac{\partial W_s(\mathbf{F})}{\partial F_{iK}} + \frac{\tilde{D}_J \tilde{D}_M}{\varepsilon \det F}\left(F_{iJ}\delta_{MK} - \frac{1}{2} F_{nJ} F_{nM} H_{iK} \right) - \Pi H_{iK} \det \mathbf{F}$$

$$\mu^s = kT\left[\log \frac{\upsilon^s C^s}{1+\upsilon^s C^s} + \frac{1}{1+\upsilon^s C^s} + \frac{\chi}{\left(1+\upsilon^s C^s\right)^2} - \sum_{b \neq s} \frac{C^b}{C^s} \right] + \Pi \upsilon^s$$ solvent

$$\mu^b = e\Phi z^b + kT \log \frac{C^b}{\upsilon^s C^s c_0^b} + \Pi \upsilon^b$$ ions

$$\tilde{E}_K = \frac{F_{iJ} F_{iK}}{\varepsilon \det \mathbf{F}} \tilde{D}_J$$

Free swelling



$$s_{iK} = \frac{\partial W_s(\mathbf{F})}{\partial F_{iK}} - \Pi H_{iK} \det \mathbf{F} = 0$$

$$\mu^s = kT\left[\log\frac{v^s C^s}{1+v^s C^s} + \frac{1}{1+v^s C^s} + \frac{\chi}{\left(1+v^s C^s\right)^2} - \sum_{b \neq s} \frac{C^b}{C^s}\right] + \Pi v^s = -2kTc_0 v^s$$

$$\mu^+ = e\Phi z^+ + kT\log\frac{C^+}{v^s C^s c_0^+} + \Pi v^+ = 0$$

$$\mu^- = e\Phi z^- + kT\log\frac{C^-}{v^s C^s c_0^-} + \Pi v^- = 0$$

Π

C^s

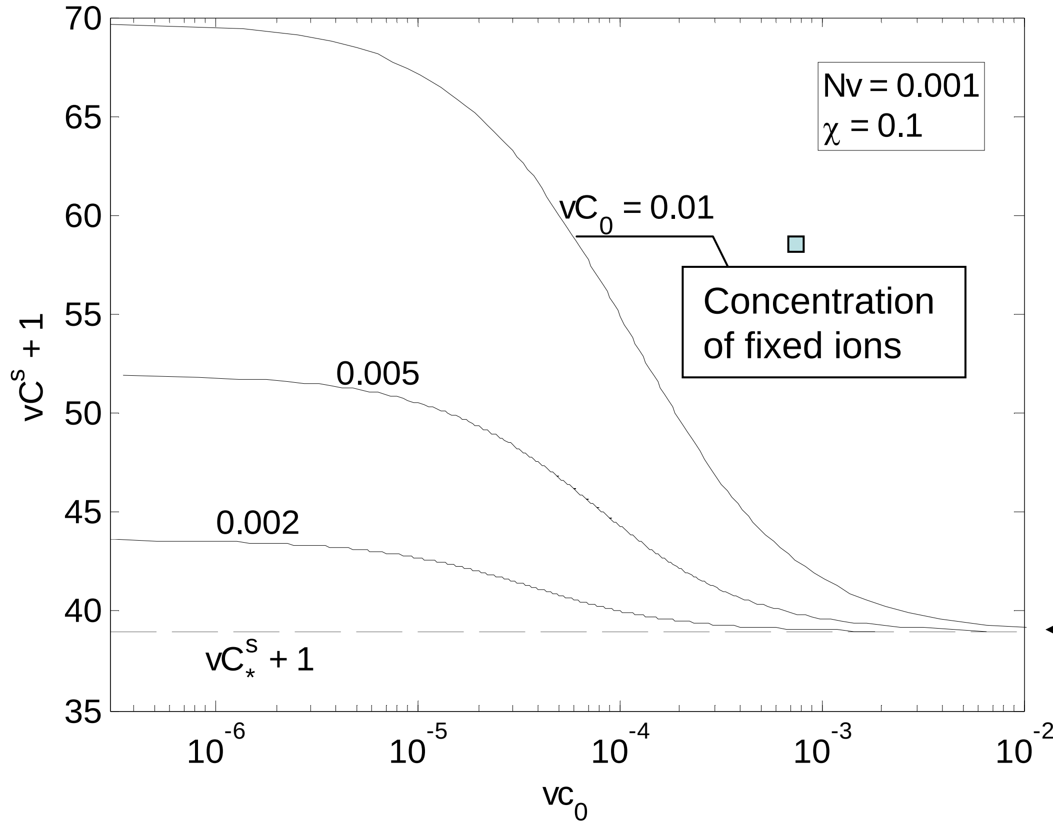
Φ

C^+

C^-

Swelling ratio

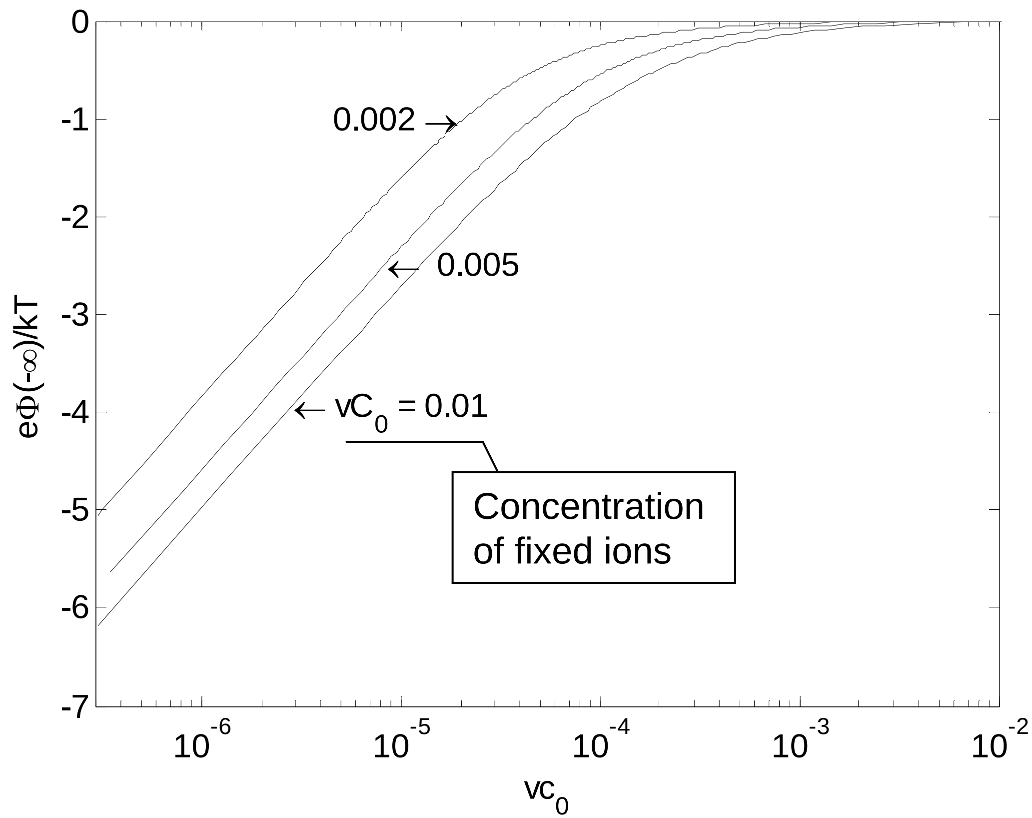
Swelling ratio



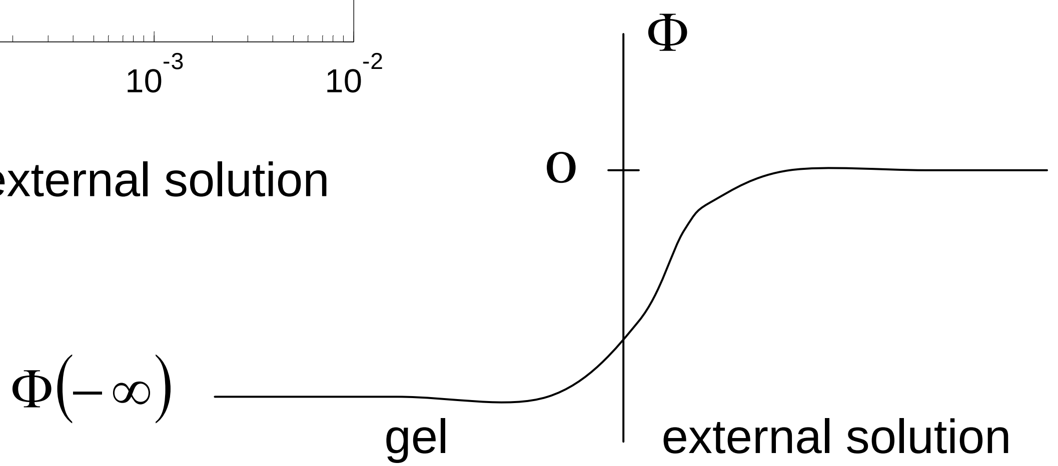
nonionic gel

Concentration of ions in external solution

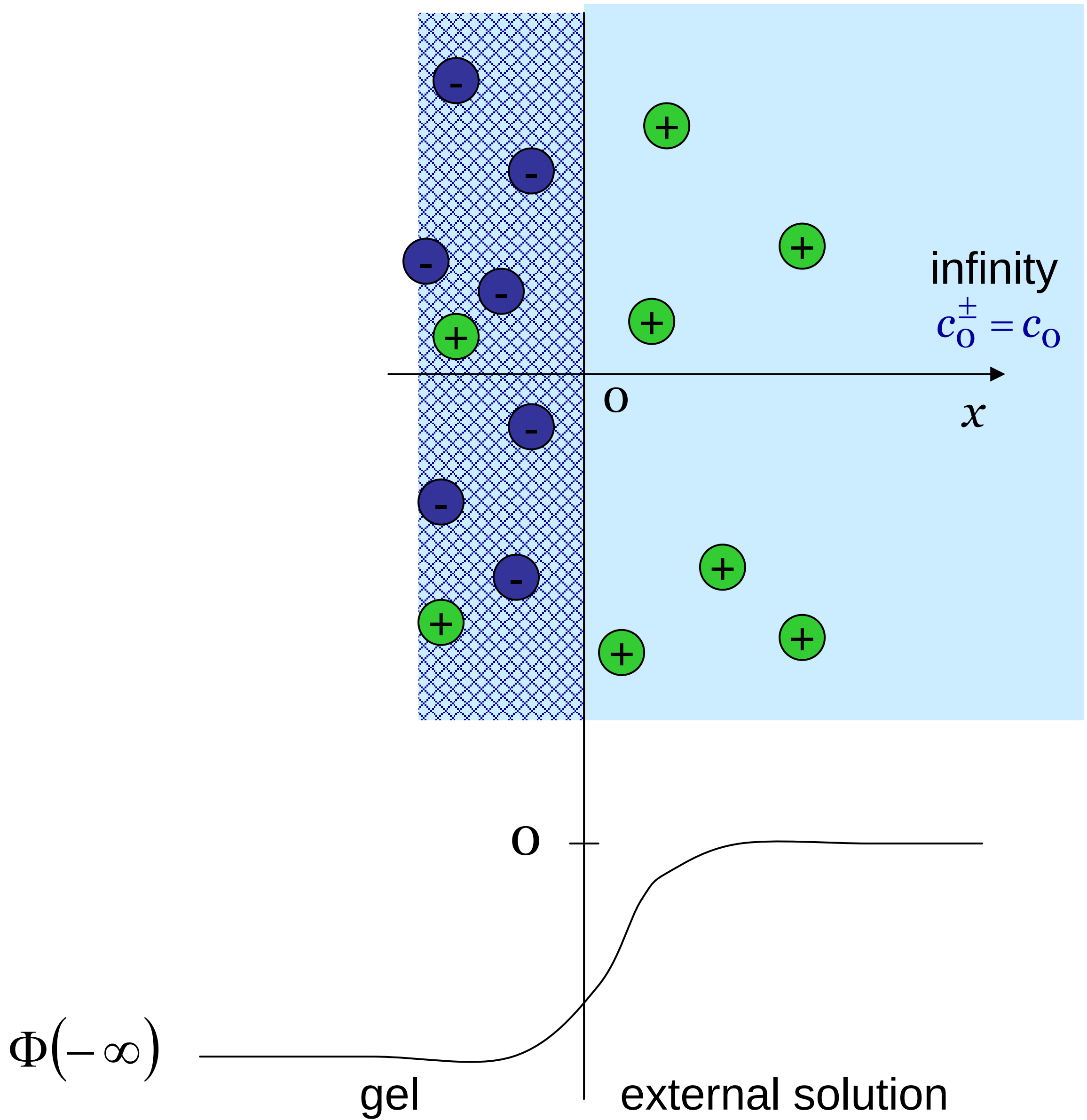
Double layer: electric potential due to free swelling



Concentration of ions in external solution



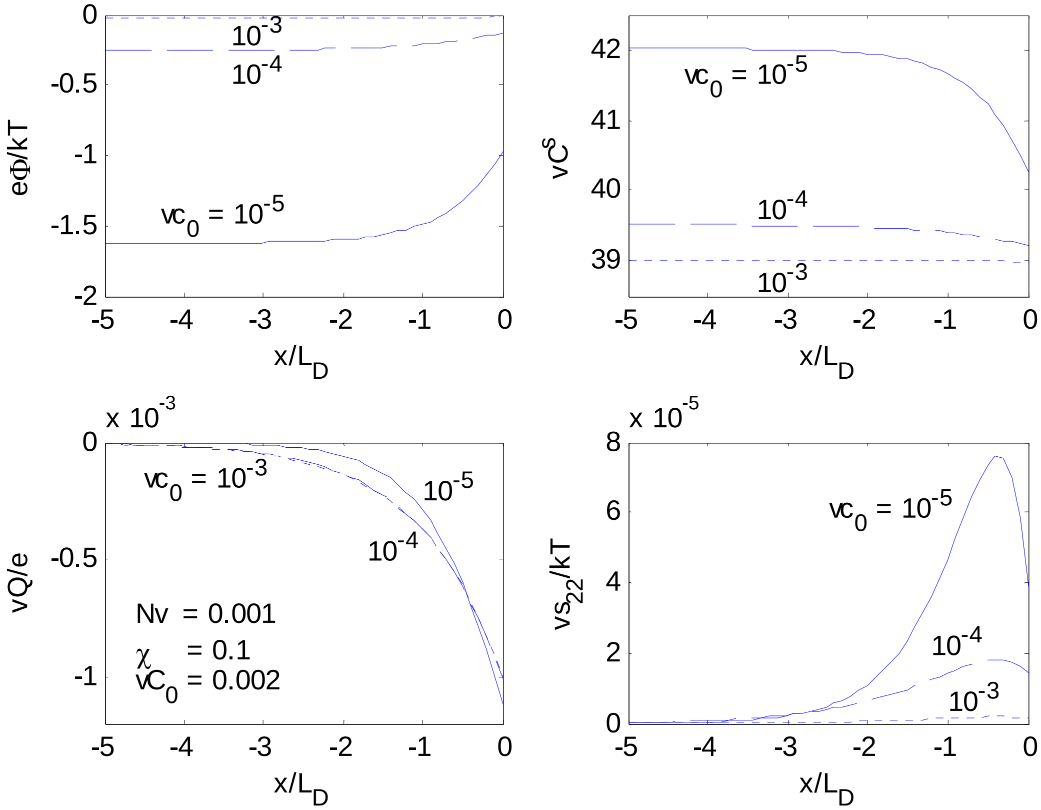
In external solution, near interface

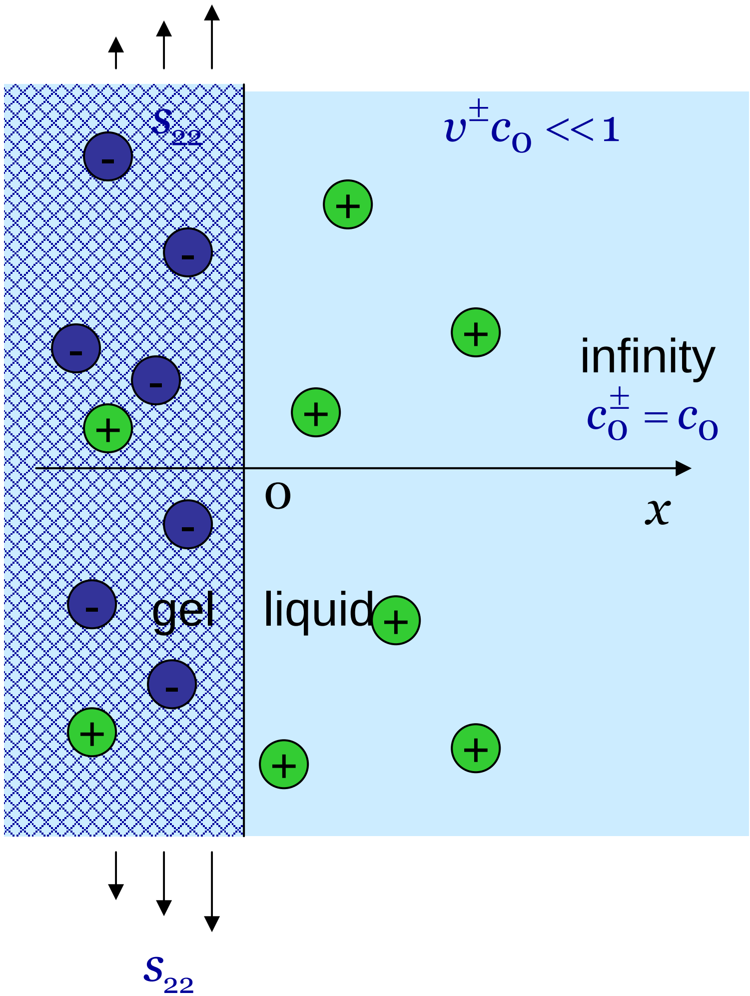


$$\Phi(x) = \Phi(o)\exp(-x/L_D)$$

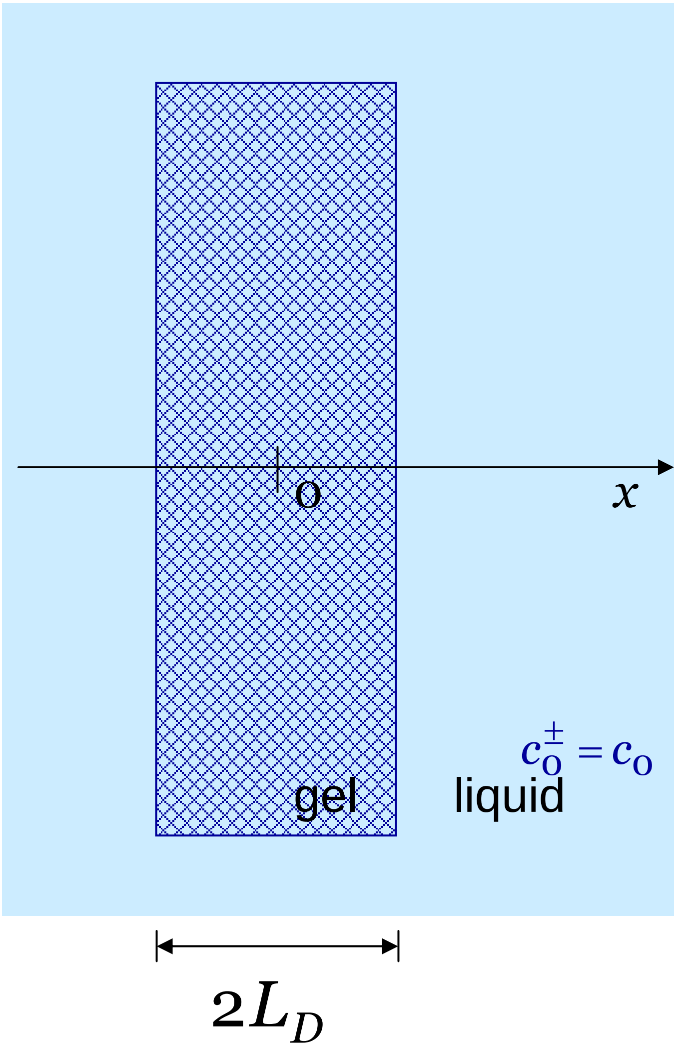
$$L_D = \sqrt{\frac{kT\varepsilon}{2e^2 c_0}}$$ Debye length

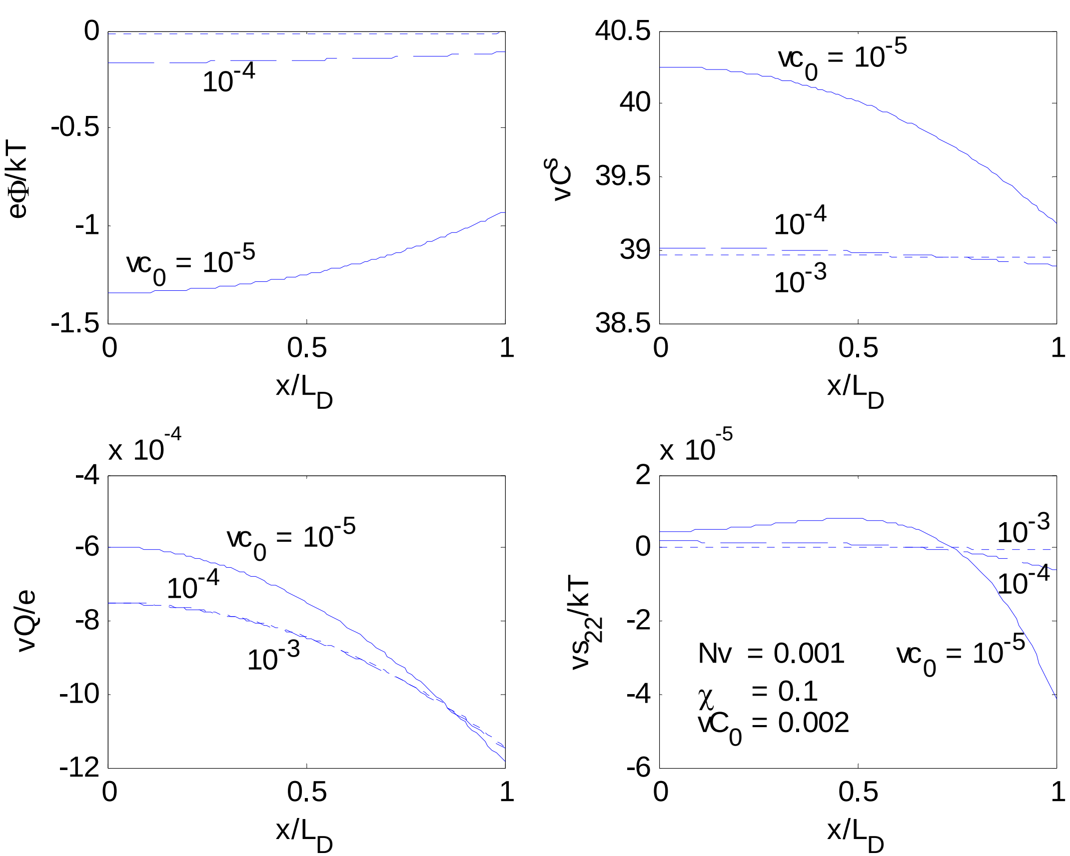
In gel, near interface



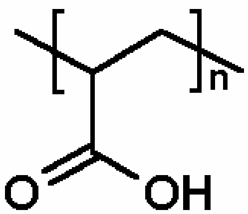


A thin layer of gel



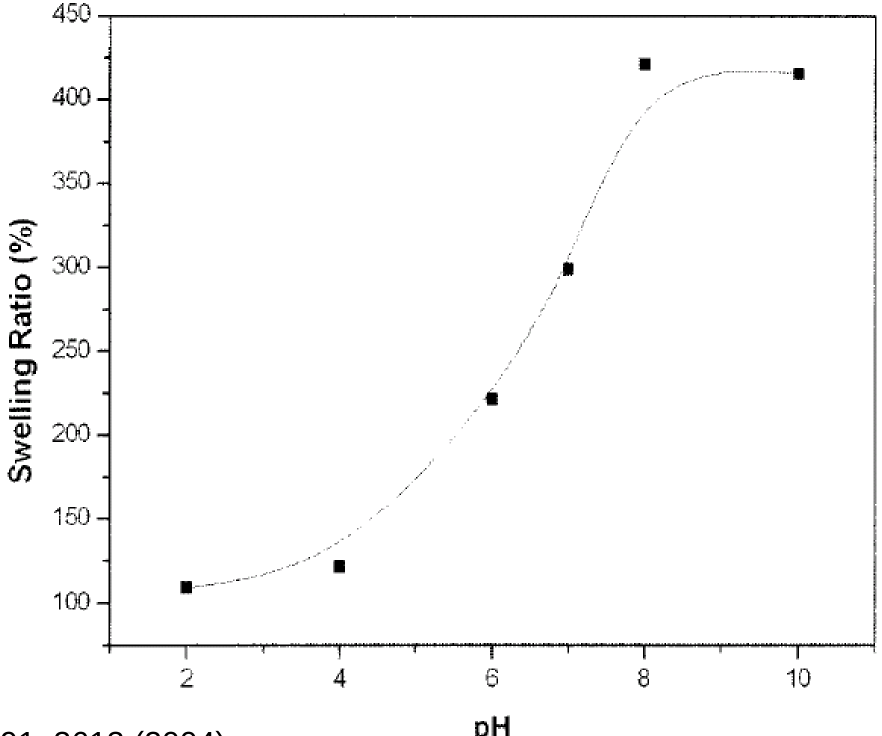


pH-sensitive gel



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

fixed mobile



Kim *et al*, J. App. Polymer. Sci., 91, 3613 (2004)

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

new variable

Conservation of H⁺ $\quad \delta C^{H^+} = \delta C_{ext}^{H^+} + \delta C^{RCOO^-}$

Conservation of charge $\quad Q = q + \sum ez^a C^a - eC^{RCOO^-}$

Equilibrium condition $\quad \int \delta W dV = \int B_i \delta x_i dV + \int T_i \delta x_i dA + \int \Phi \delta q dV + \int \Phi \delta \omega dA + \sum_a \mu^a \int \delta C_{ext}^a dV$

Helmholtz free energy $\quad W = W\left(\mathbf{F}, \tilde{\mathbf{D}}, C^s, C^{H^+}, C^{Cl^-}, C^{RCOO^-}\right)$

$$\Downarrow$$

$$\boxed{\mu^{H^+} = e\Phi + \frac{\partial W}{\partial C^{H^+}}} \qquad \boxed{\mu^{Cl^-} = -e\Phi + \frac{\partial W}{\partial C^{Cl^-}}} \qquad \boxed{\frac{\partial W}{\partial C^{H^+}} + \frac{\partial W}{\partial C^{RCOO^-}} = 0}$$

Free-energy function

$$W\left(\mathbf{F},\tilde{\mathbf{D}},C^s,C^{H^+},C^{Cl^-},C^{RCOO^-}\right)=W_s(\mathbf{F})+W_m\left(C^s,C^{H^+},C^{Cl^-}\right)+W_p\left(\mathbf{F},\tilde{\mathbf{D}}\right)+W_d\left(C^{RCOO^-}\right)$$

Free energy of dissociation

$$W_d\left(C^{RCOO^-}\right)=\underbrace{kT\left[C^{RCOO^-}\ln\frac{C^{RCOO^-}}{C_0^{RCOOH}}+\left(C_0^{RCOOH}-C^{RCOO^-}\right)\ln\left(1-\frac{C^{RCOO^-}}{C_0^{RCOOH}}\right)\right]}_{\text{Entropy of mixing between RCOO}^-\text{ and RCOOH}}-\gamma C^{RCOO^-}$$

Entropy of mixing between RCOO- and RCOOH

Enthalpy of dissociation

In equilibrium

$$\ln\frac{C^{H^+}}{\upsilon^s C^s c_0^{H^+}}+\ln\frac{C^{RCOO^-}}{C_0^{RCOOH}-C^{RCOO^-}}-\frac{\gamma}{kT}=0$$

$$C^{RCOO^-}=\frac{K_d C_0^{RCOOH}}{K_d+\dfrac{C^{H^+}}{C^s}}$$

$$K_d=\upsilon^s c_0^{H^+}\exp\left(-\frac{\gamma}{kT}\right)$$

Summary

- Couple mechanics and electrochemistry.
- Maxwell stress emerges under ideal dielectric assumption
- Free swelling.
- Double layer at interface.
- Future work: relate to experiments; analyze interesting phenomena.