Mechanics of Soft Active Materials (SAMs)

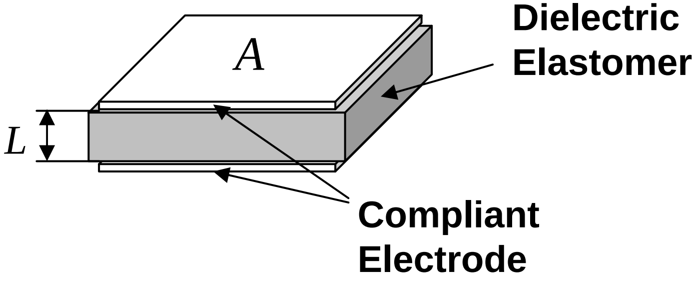
Zhigang Suo
Harvard University

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

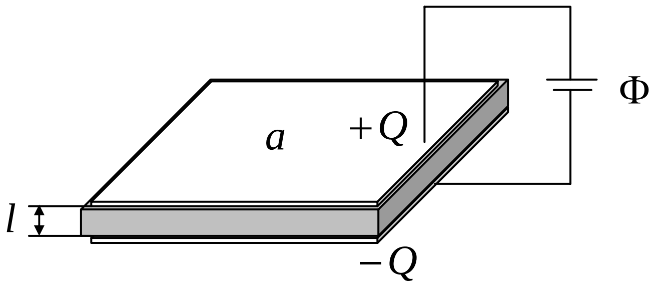
Active: large deformation in response to diverse stimuli
(e.g., electric field, temperature, pH, salt)

Dielectric elastomer: electrostatics meets mechanics

Reference State

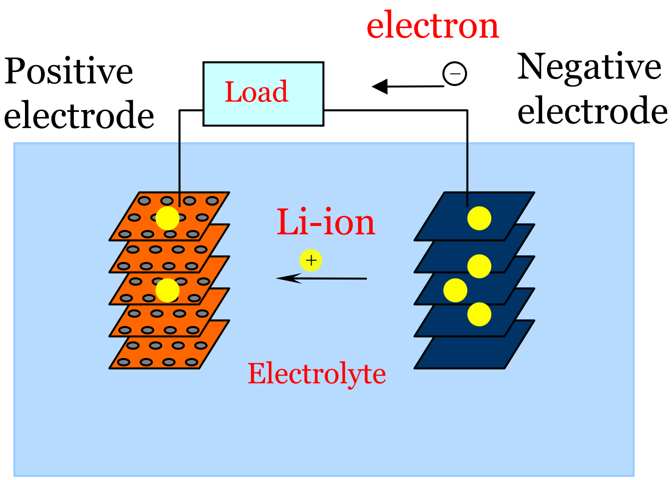


Current State

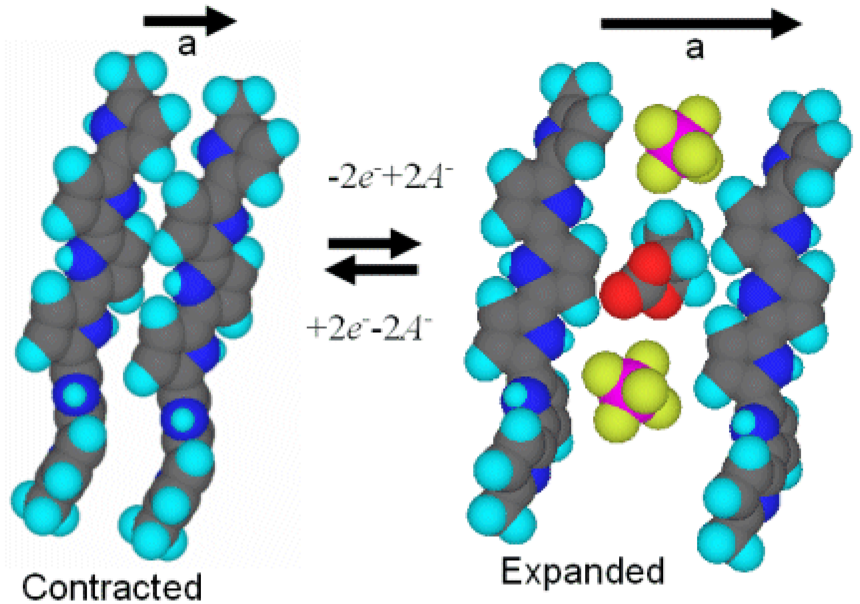


Pelrine, Kornbluh, Pei, Joseph
High-speed electrically actuated elastomers with strain greater than 100%.
Science 287, 836 (2000).

Insertion reaction: electrochemistry meets mechanics

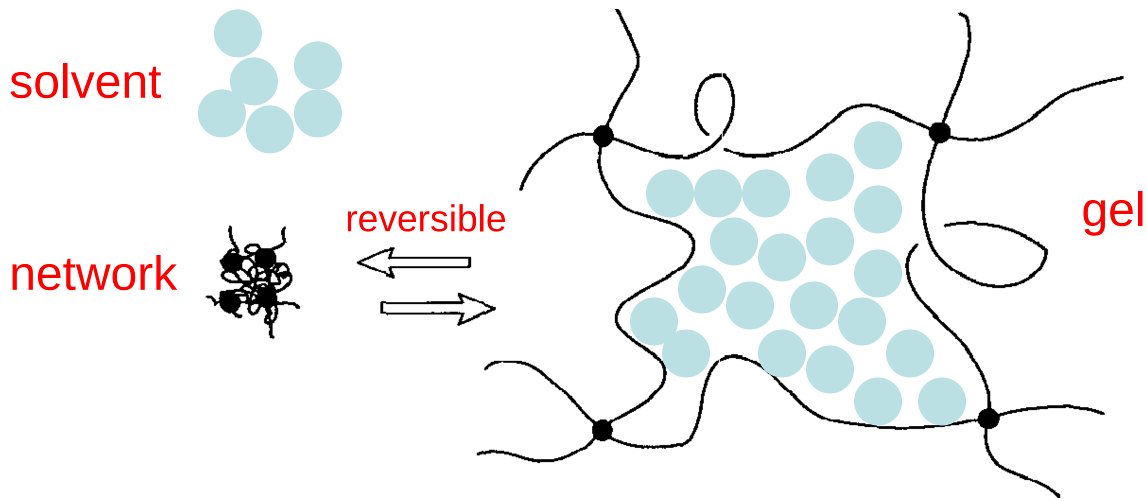


Lithium-ion battery

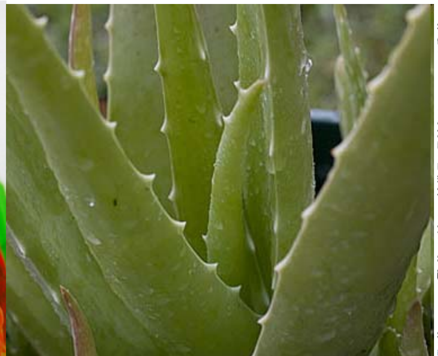
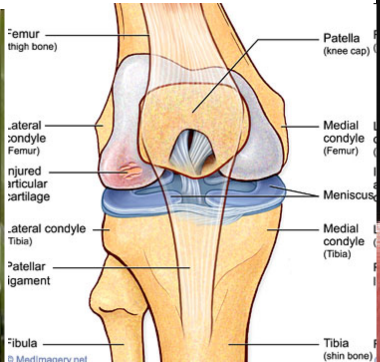


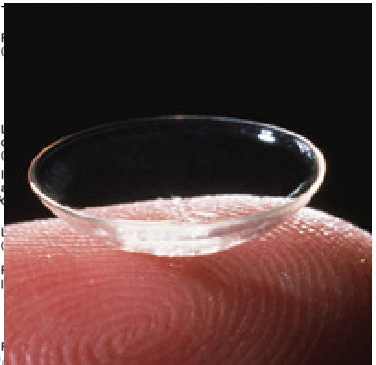
Conducting polymers

gel = network + solvent



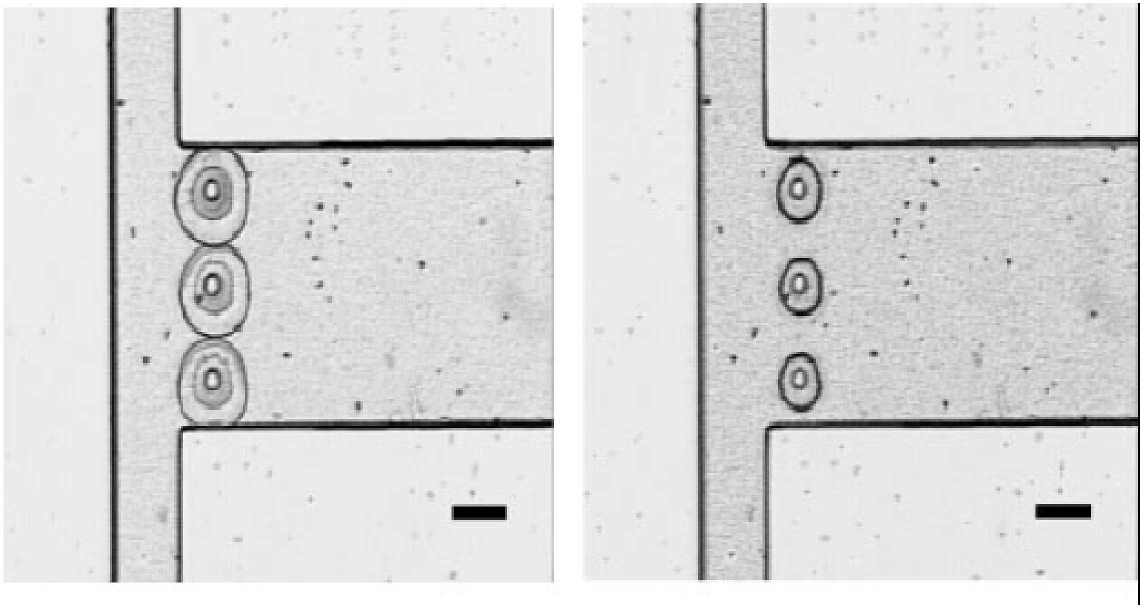
Solid-like: long polymers crosslink by strong bonds. Retain shape
Liquid like: polymers and solvent aggregate by weak bonds. Enable transport



Valve in microfluidics

David Beebe



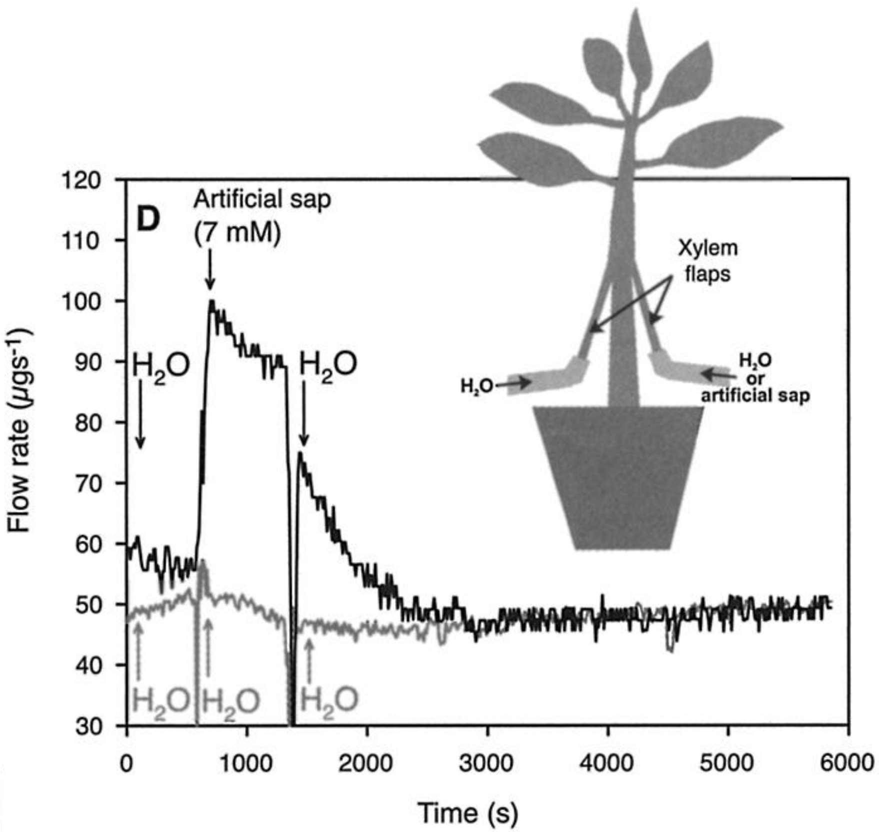
Responsive to Physiological variables:

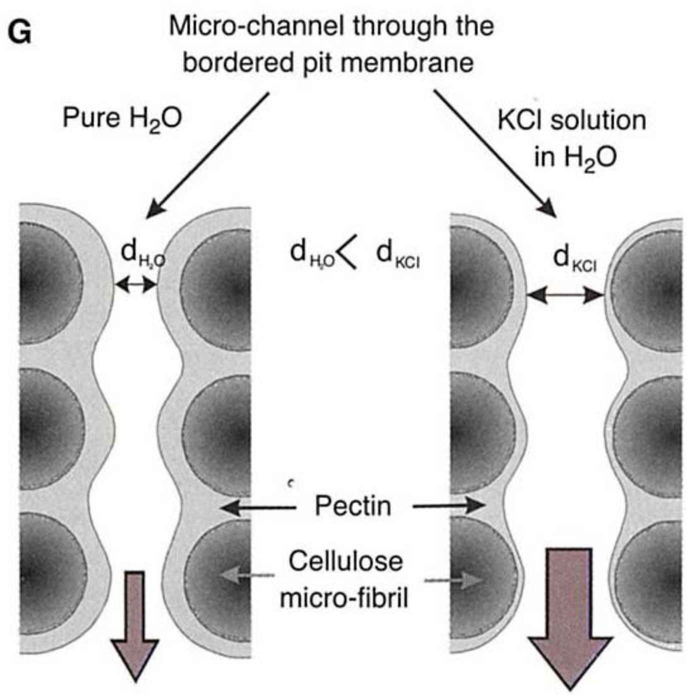
- •pH
- •Salt
- •Temperature
- •light

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

Gels regulate flow in plants

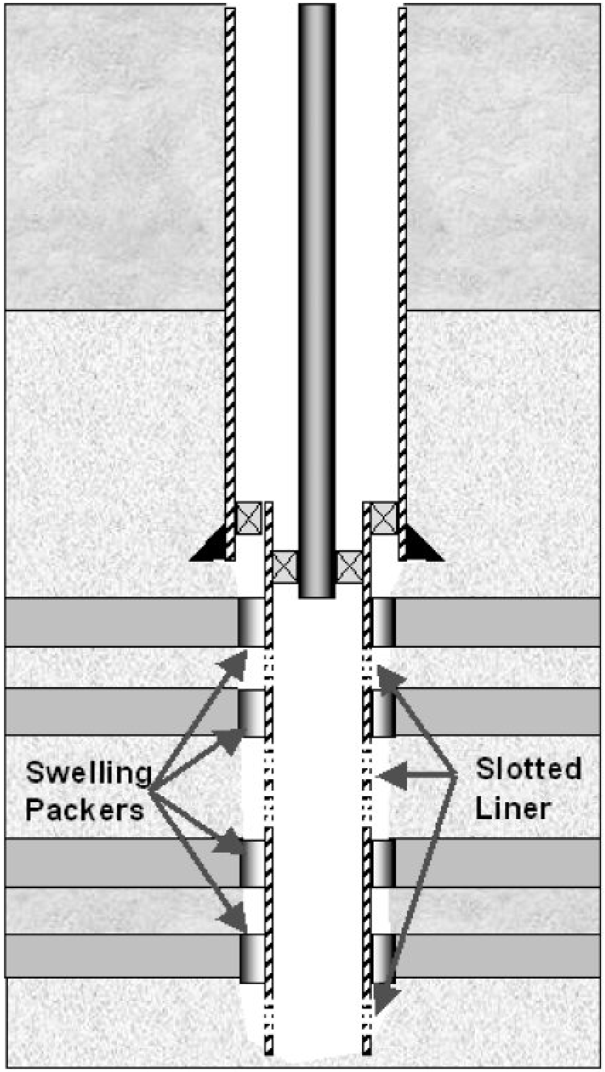
Missy Holbrook





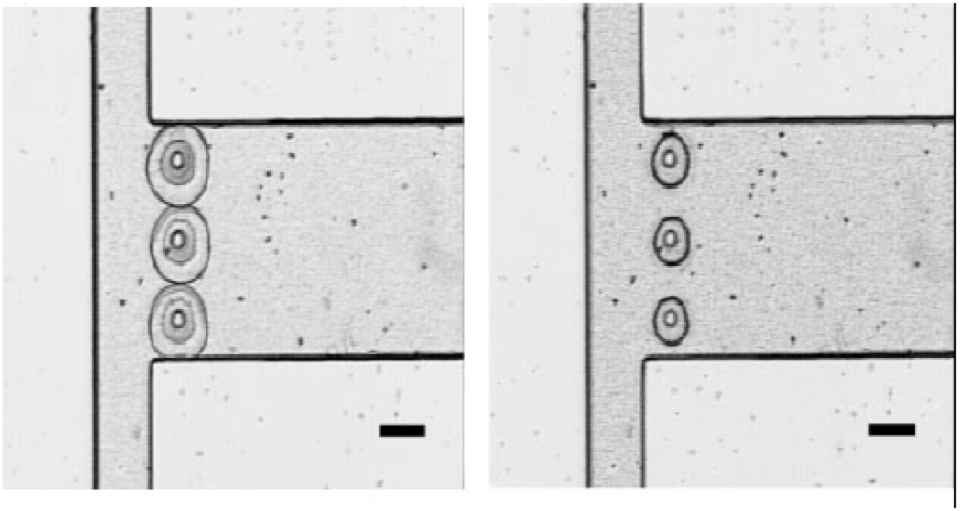
Zwieniecki, Melcher, Holbrook,
Hydrogel control of xylem hydraulic resistance in plants
Science 291, 1095 (2001)

Swelling packers in oil wells



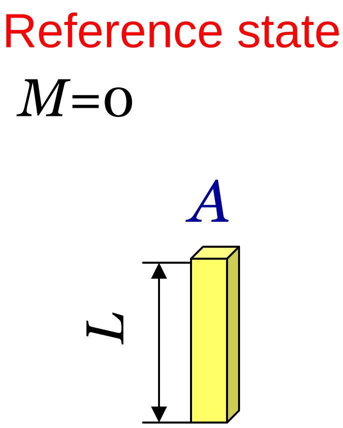
Gels as transducers

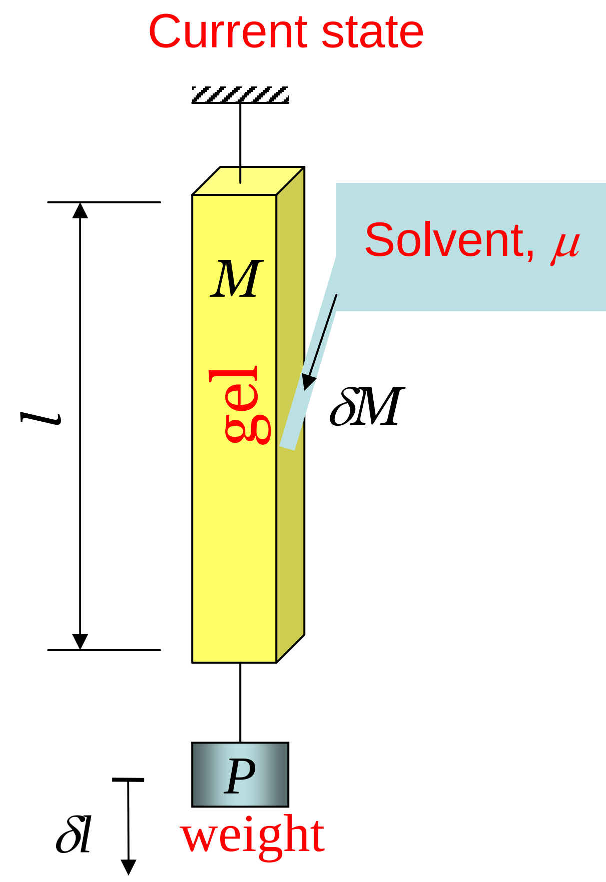
- A swelling gel is blocked by a hard material.
- Blocking force.
- Inhomogeneous deformation.



Need to formulate boundary-value problems

2 ways of doing work





Equilibrium condition

$$\delta F = P\delta l + \mu \delta M$$

$$\frac{\delta F}{AL} = \frac{P}{A}\frac{\delta l}{L} + \mu \frac{\delta M}{AL}$$

$$\delta W = s\delta\lambda + \mu \delta C$$

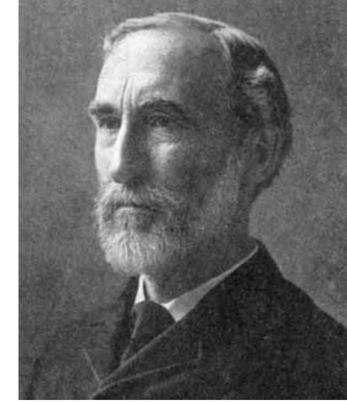
$W(\lambda, C)$ Helmholtz free energy per volume

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

$$s = \frac{P}{A}$$

$$C = \frac{M}{AL}$$

Inhomogeneous field



Gibbs (1878)

Deformation gradient

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

Concentration

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

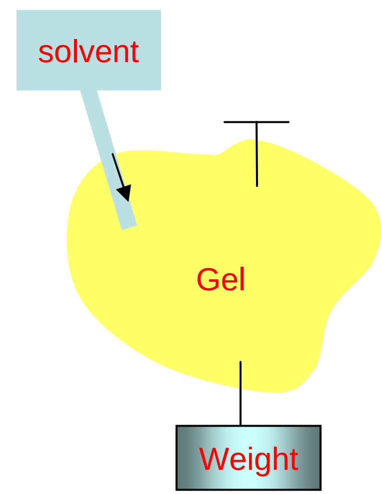
Free-energy function

$$W(\mathbf{F},C)$$

Condition of equilibrium

$$\int \delta W dV = \int B_i \delta x_i dV + \int T_i \delta x_i dA + \mu \int \delta C dV$$

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



1. How to solve boundary-value problems?
2. How to prescribe $W(\mathbf{F},C)$?
3. What boundary-value problems to solve?

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

Finite element method

Equilibrium condition $\int \delta W dV = \int B_i \delta x_i dV + \int T_i \delta x_i dA + \mu \int \delta C dV$

Legendre transform $\hat{W}(\mathbf{F}, \mu) = W - \mu C$

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

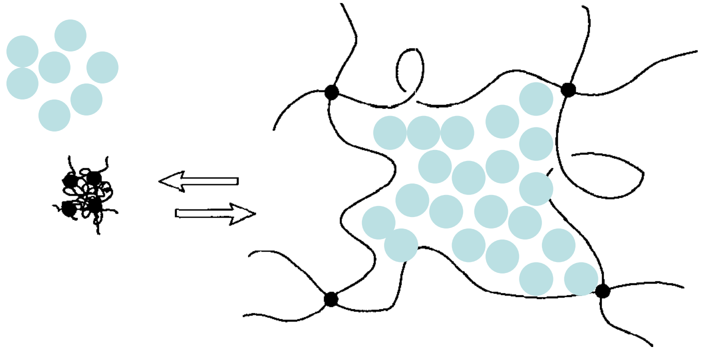
- A gel in equilibrium is analogous to an elastic solid
- ABAQUS UMAT

Hong, Liu, Suo, Int. J. Solids Structures 46, 3282 (2009)

Free-energy function

Paul Flory

- Swelling decreases entropy by straightening polymers.
- Swelling increases entropy by mixing solvent and polymers.



Free-energy function $$W(\mathbf{F},C)=W_s(\mathbf{F})+W_m(C)$$

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 $$W_m(C)=-\frac{kT}{v}\left[vC\log\left(1+\frac{1}{vC}\right)+\frac{\chi}{1+vC}\right]$$

Adding volume $$1+vC=\det\mathbf{F}$$

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

Stress-strain relation

$$\sigma_1 = \frac{NkT\left(\lambda_1^2 - 1\right)}{\lambda_2 \lambda_3 \lambda_3} - \Pi$$

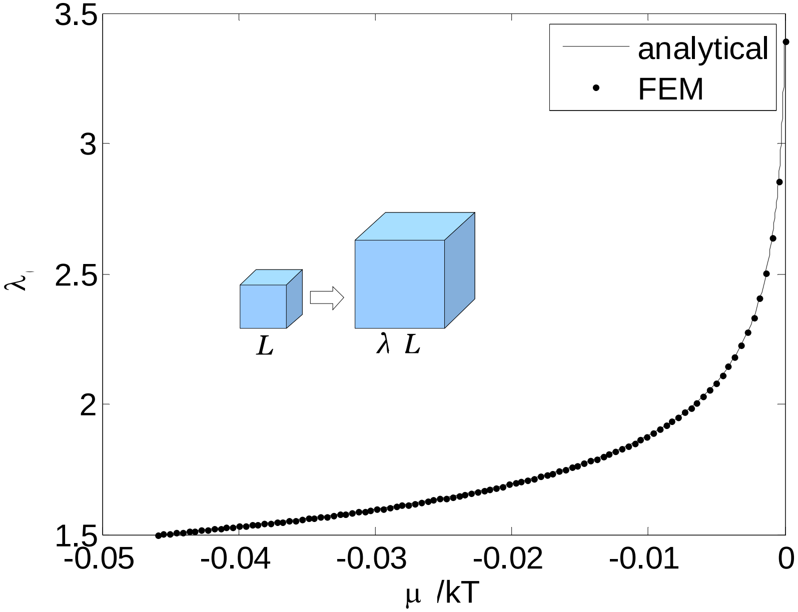
$$\sigma_2 = \frac{NkT\left(\lambda_2^2 - 1\right)}{\lambda_2 \lambda_3 \lambda_3} - \Pi$$

$$\sigma_3 = \frac{NkT\left(\lambda_3^2 - 1\right)}{\lambda_2 \lambda_3 \lambda_3} - \Pi$$

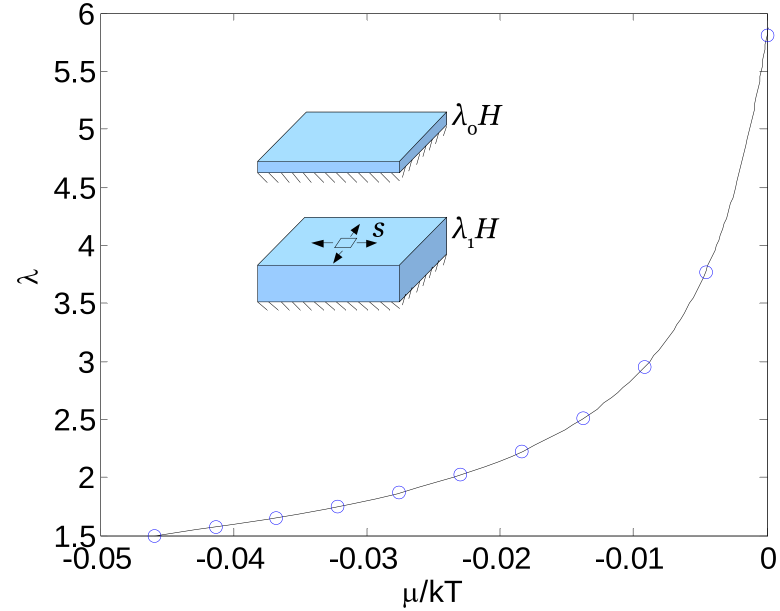
$$\Pi = \frac{\mu}{v} - \frac{kT}{v}\left[\log\left(1 - \frac{1}{\lambda_2 \lambda_3 \lambda_3}\right) + \frac{1}{\lambda_2 \lambda_3 \lambda_3} + \frac{\chi}{\left(\lambda_2 \lambda_3 \lambda_3\right)^2}\right]$$

Anisotropic swelling

Free swelling



Unidirectional swelling

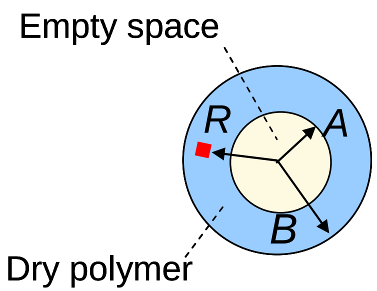


A gel imbibes a different amount of solvent under constraint.

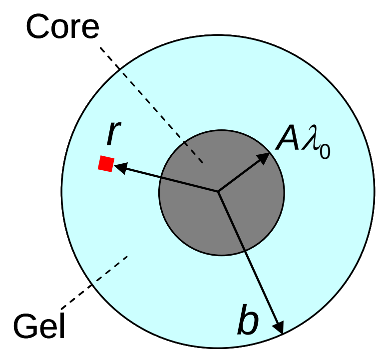
$$(\lambda_{\text{free}})^3 \neq \lambda_{\text{unidirectional}}$$

Treloar, Trans. Faraday Soc. 46, 783 (1950).

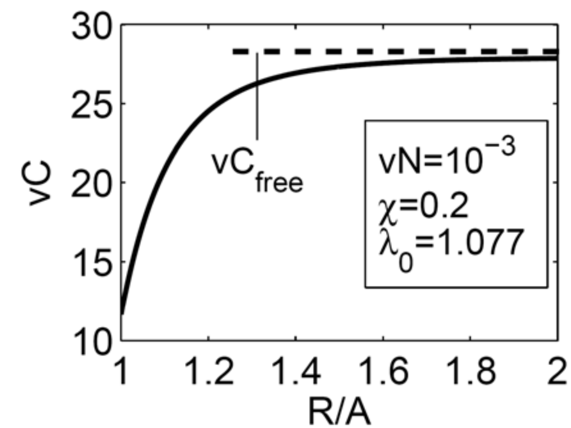
Inhomogeneous swelling

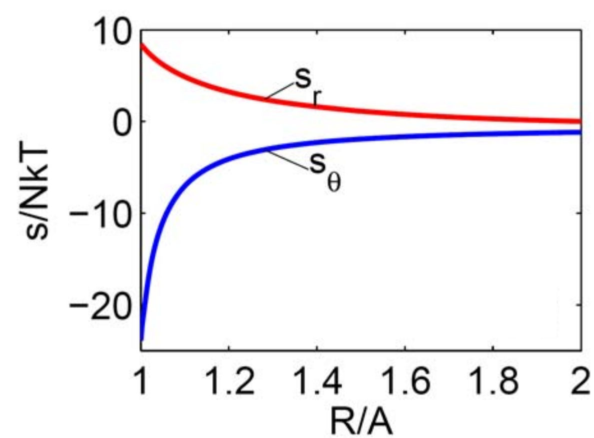


Reference State



Equilibrium State





- Concentration is inhomogeneous even in equilibrium.
- Stress is high near the interface (debond, cavitation).

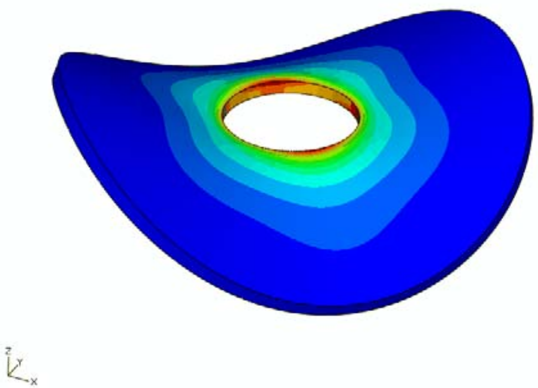
Sternstein, J. Macromolol. Soc. Phys. B6, 243 (1972)

Zhao, Hong, Suo, APL 92, 051904 (2008)

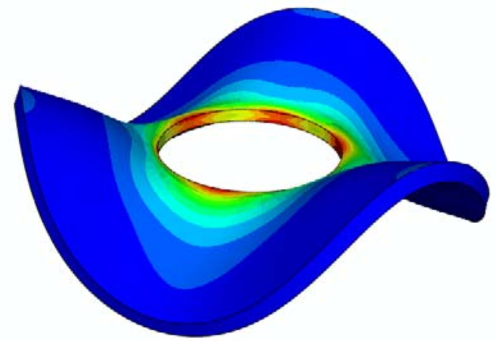
Swelling-induced buckling

$R_O / H = 15$

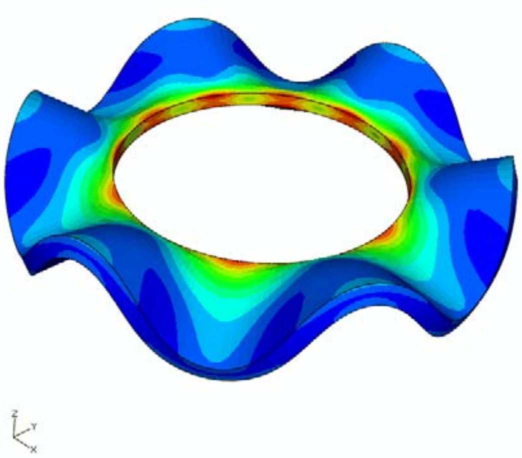
$R_i / H = 5$



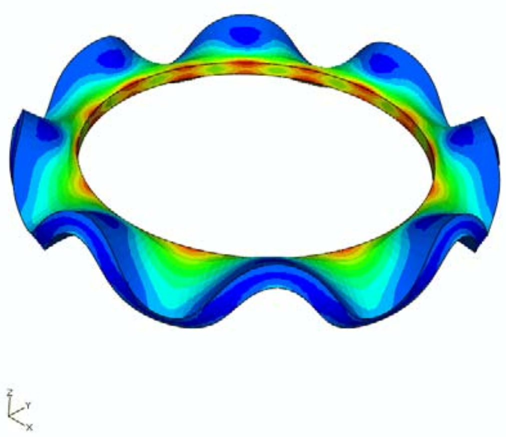
$R_i / H = 7$



$R_i / H = 10$

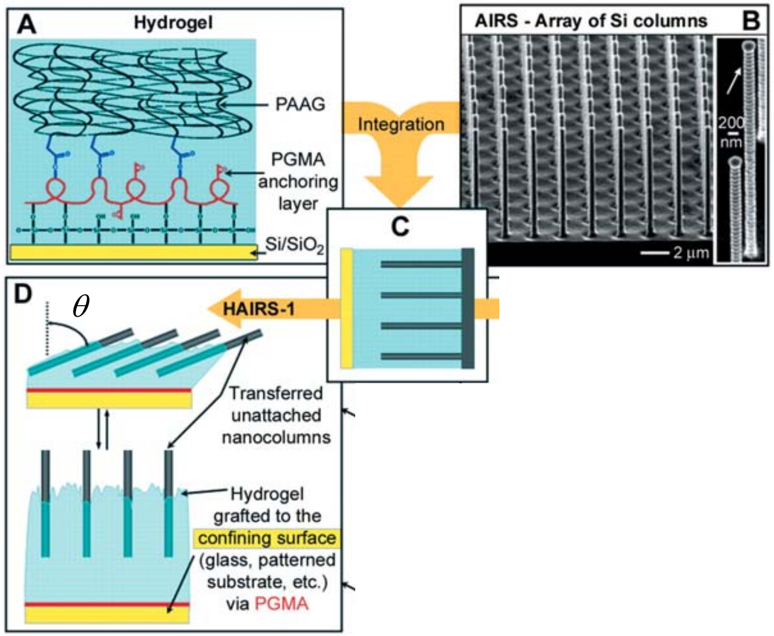


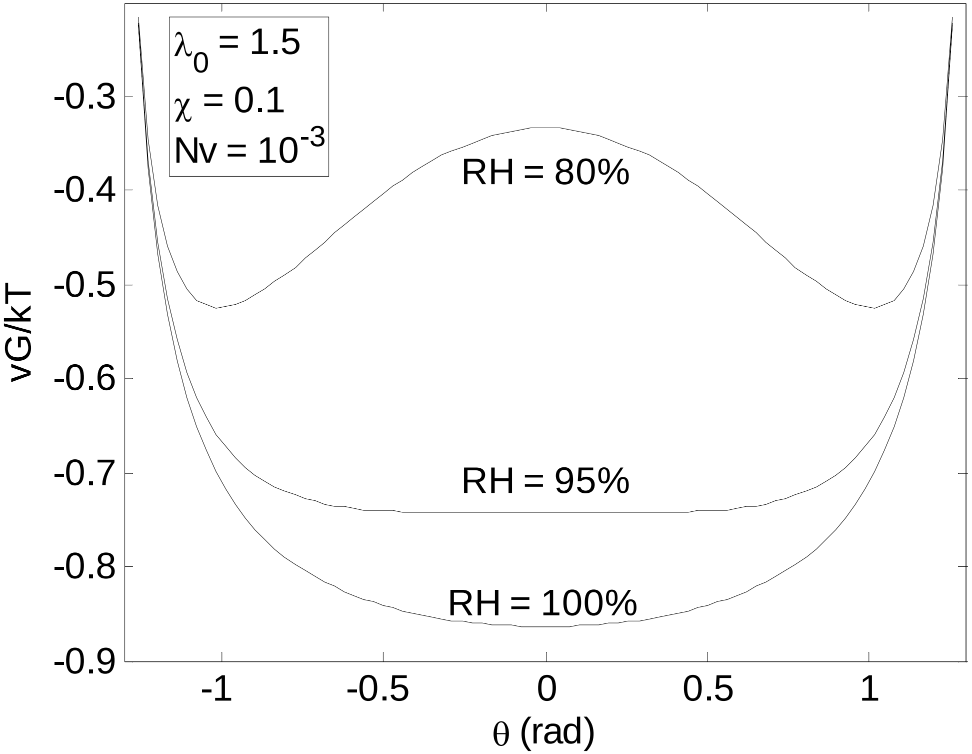
$R_i / H = 12$



Gel and nano-rods

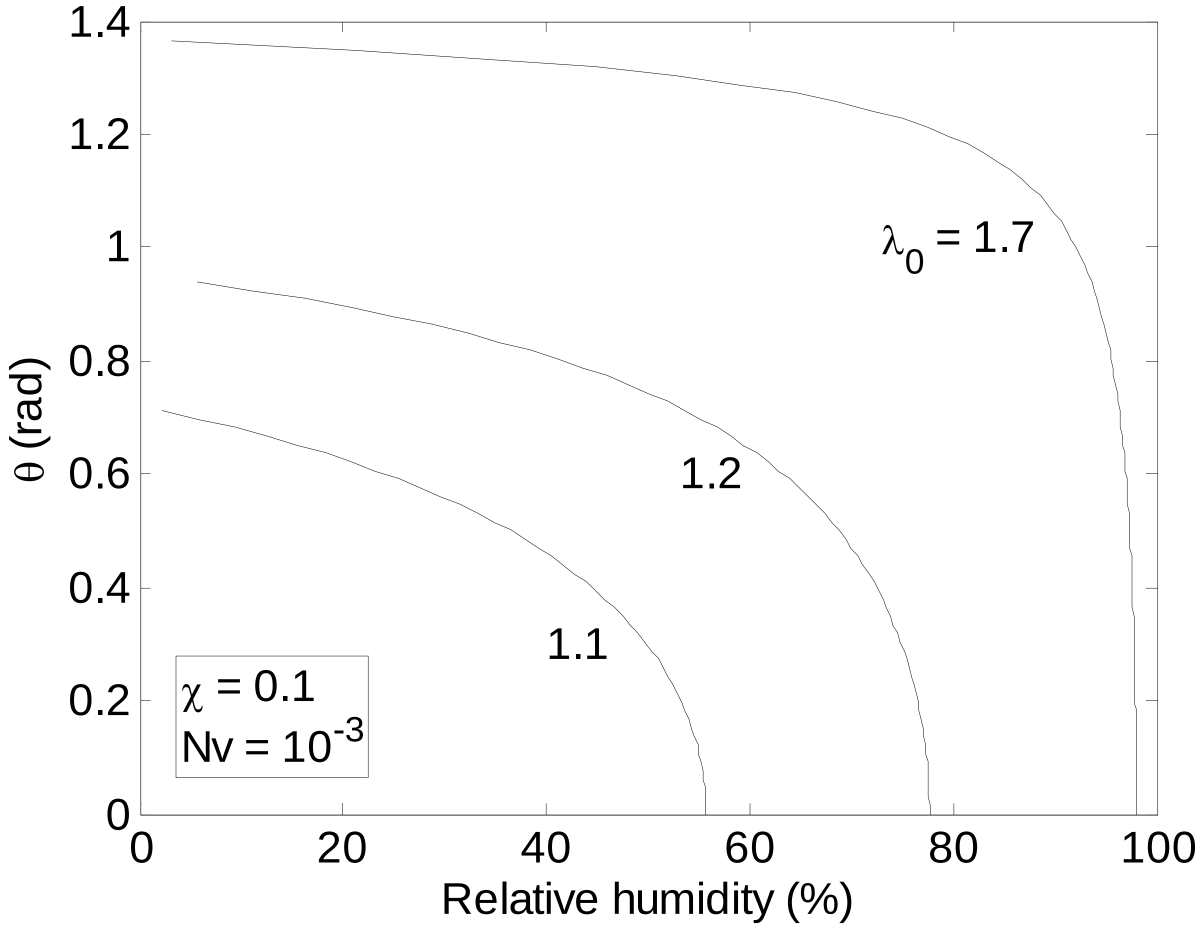
Joanna Aizenberg





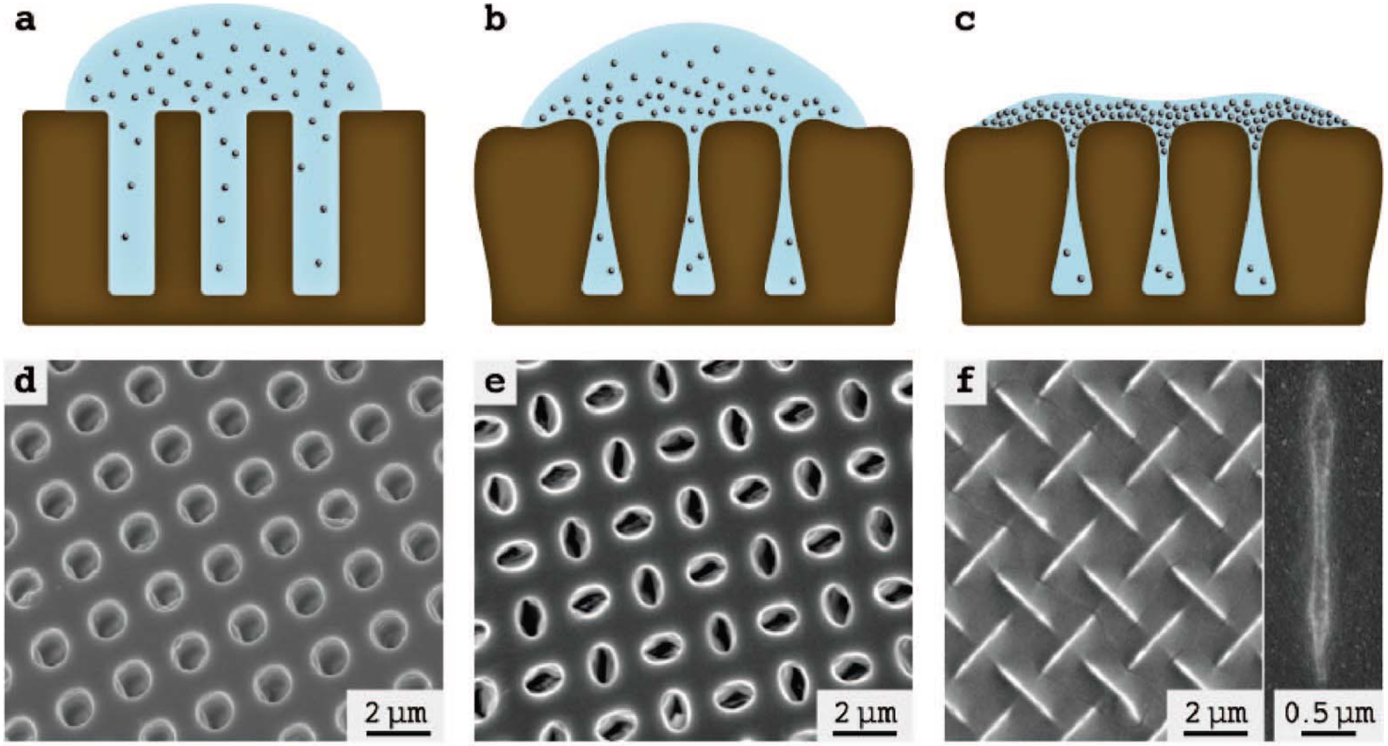
Experiment: Sidorenko, Krupenin, Taylor, Fratzl, Aizenberg, Science 315, 487 (2007).
Theory: Hong, Zhao, Suo, JAP104, 084905 (2008) .

Critical humidity can be tuned



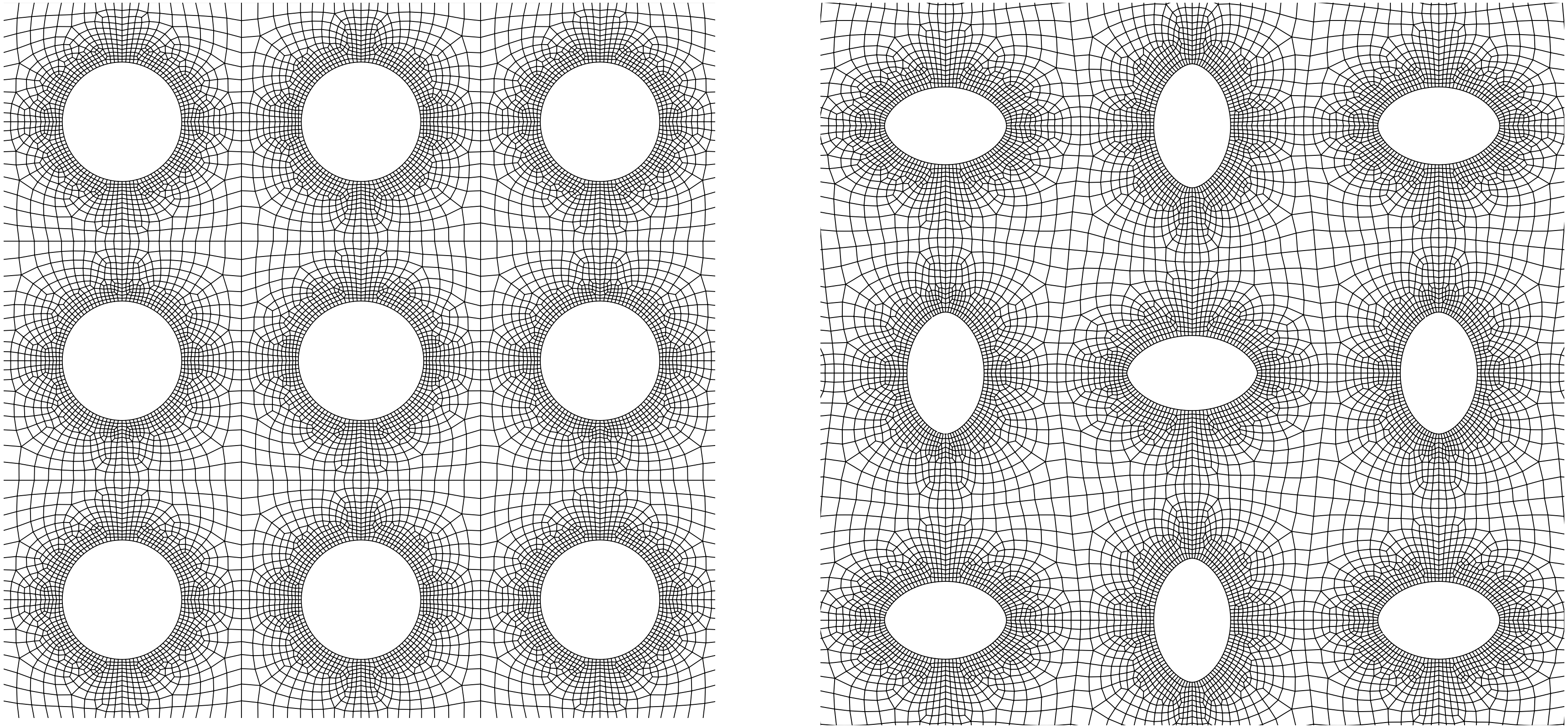
Swelling-induced bifurcation

Shu Yang



Zhang, Matsumoto, Peter, Lin, Kamien, Yang, Nano Lett. 8, 1192 (2008).

Swelling-induced bifurcation



Experiment: Zhang, Matsumoto, Peter, Lin, Kamien, Yang, Nano Lett. 8, 1192 (2008).
Simulation: Hong, Liu, Suo, Int. J. Solids Structures 46, 3282 (2009)

Crease

Liang Fen (凉粉), a starch gel
A food popular in northern China

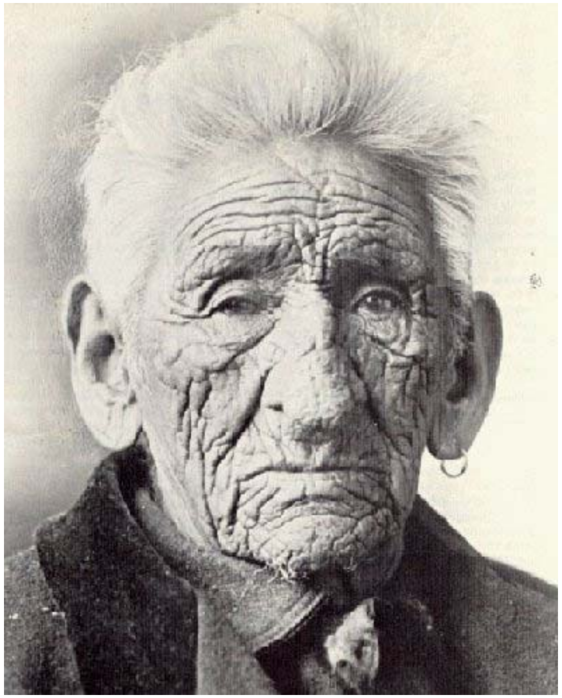
Dough

Zhigang, I was making bread this weekend, and realized that when the rising dough was constrained by the bowl it formed the creases that you were talking about in New Orleans.

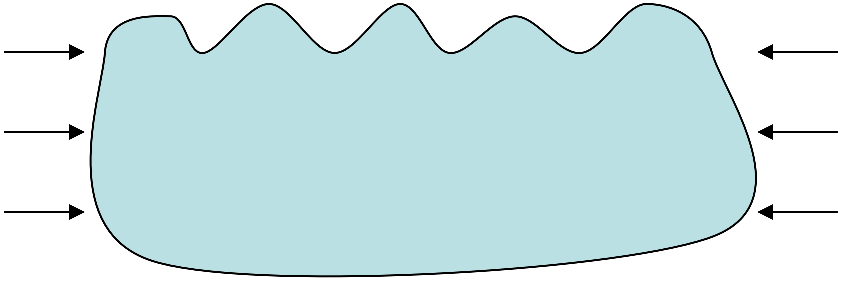
-- An email from **Michael Thouless**

Brain

Face



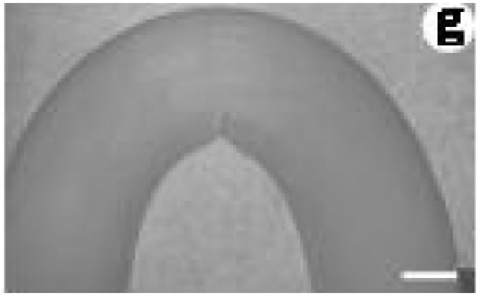
Crease: theory and experiment



Biot, Appl. Sci. Res. A 12, 168 (1963).
Theory: linear perturbation analysis

$\varepsilon_{\text{Biot}} \approx 0.46$

Maurice Biot



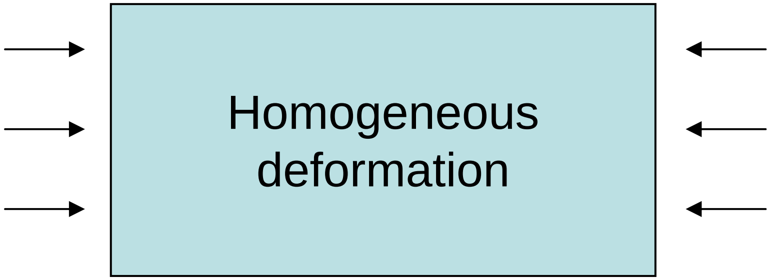
Gent, Cho, Rubber Chemistry and Technology 72, 253 (1999)
Ghatak, Das, PRL 99, 076101 (2007)
Experiments: bending rods of rubber and gel

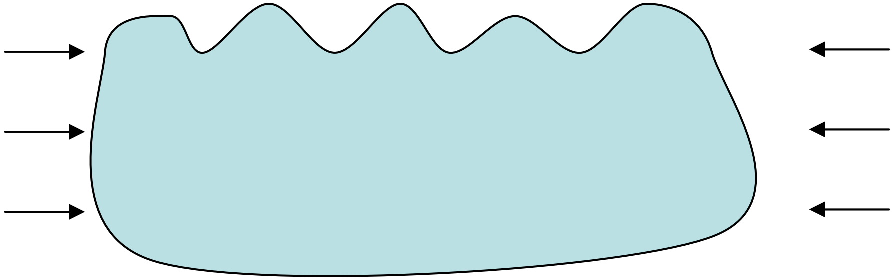
$\varepsilon_{\text{Gent}} \approx 0.35$

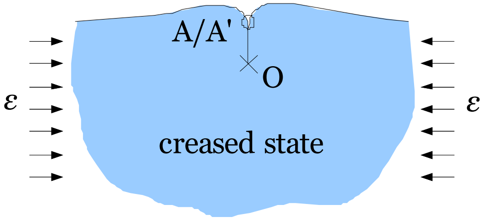
Alan Gent

What's wrong with Biot's theory?

Mahadevan





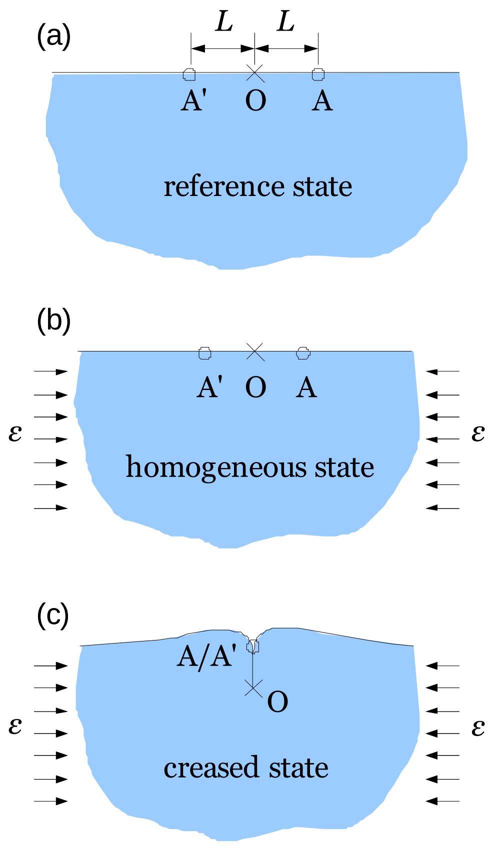


Biot's theory: infinitesimal strain
from the state of homogeneous deformation

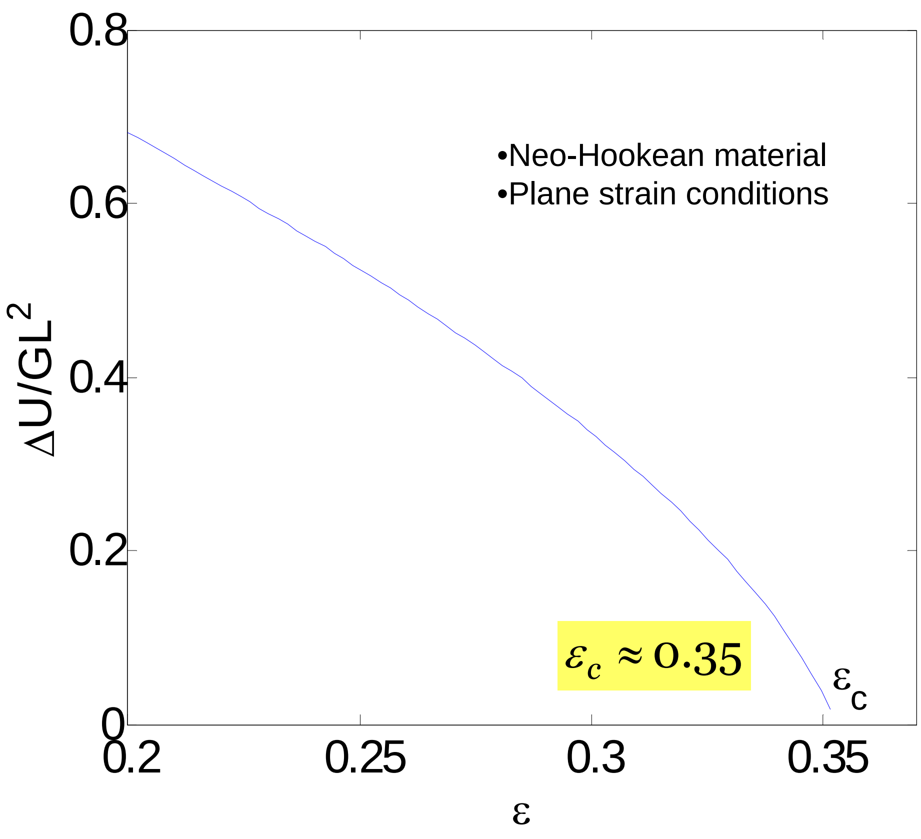
Crease: Large strain
from the state of homogeneous deformation

Hohlfeld, Mahadevan (2008):
crease is an instability different from that analyzed by Biot.

An energetic model of crease

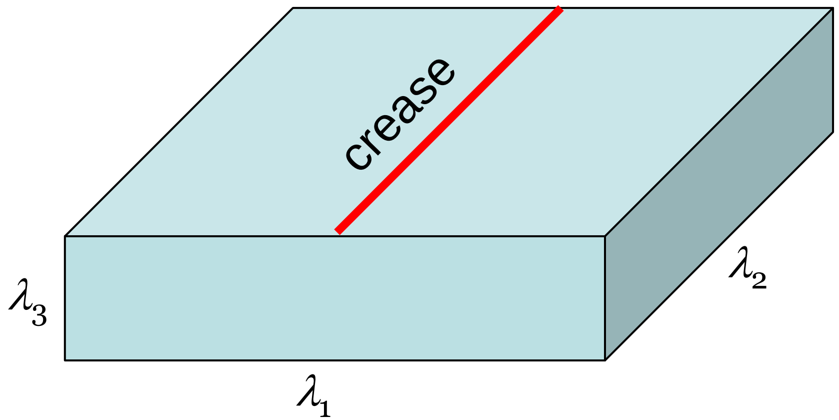


$$\Delta U = L^2 G f(\varepsilon)$$



Hong, Zhao, Suo, http://imechanica.org/node/5999

Crease under general loading



Incompressibility

$\lambda_1 \lambda_2 \lambda_3 = 1$

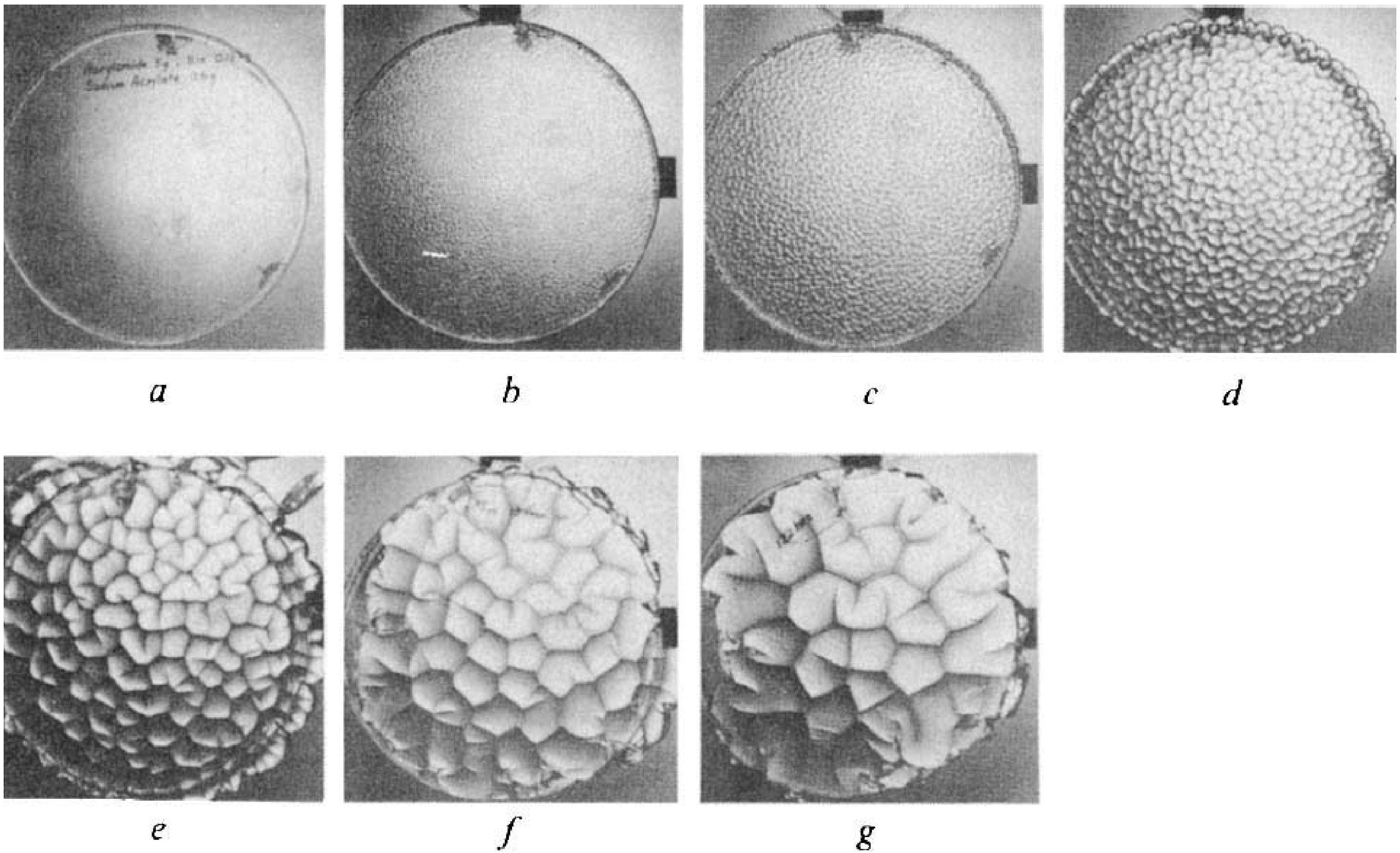
Critical condition for crease $\lambda_3 / \lambda_1 = 2.4$

Biot $\lambda_3 / \lambda_1 = 3.4$

Hong, Zhao, Suo, http://imechanica.org/node/5999

Crease of a gel during swelling

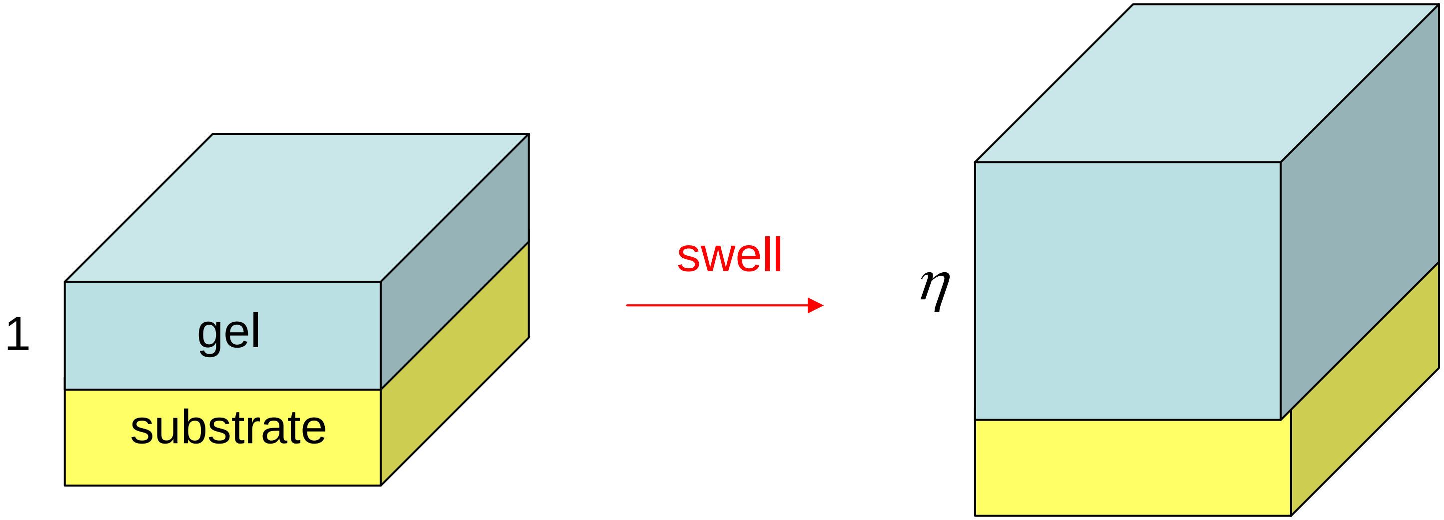
Toyoichi Tanaka
1946-2000



Tanaka *et al*, Nature 325, 796 (1987)

Crease of a swelling gel

Ryan Hayward



Theories

$$\eta_c = 2.4$$

$$\eta_{\text{biot}} = 3.4$$

Experimental data

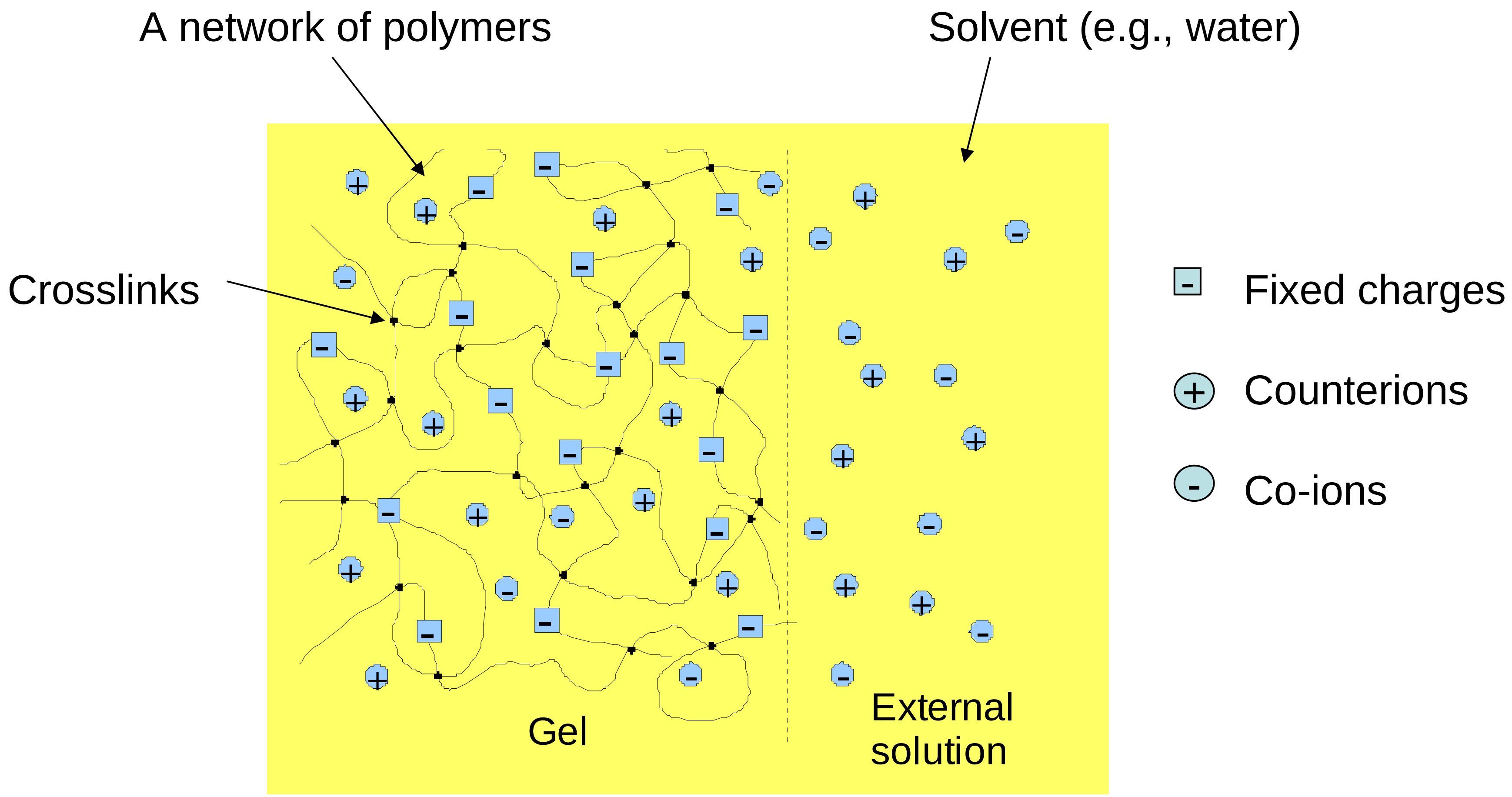
Southern, Thomas, J. Polym. Sci., Part A, 3, 641 (1965) $\eta_{\text{exp}} = 2.4$

Tanaka, PRL 68, 2794 (1992) $\eta_{\text{exp}} = 2.5 - 3.7$

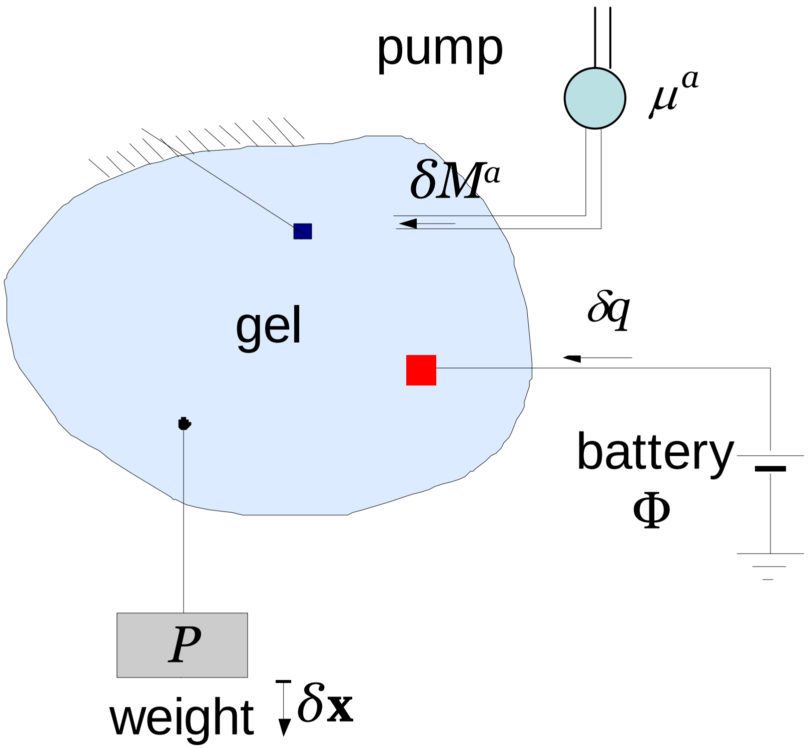
Trujillo, Kim, Hayward, Soft Matter 4, 564 (2008) $\eta_{\text{exp}} = 2.0$

Hong, Zhao, Suo, http://imechanica.org/node/5999

Polyelectrolyte gels



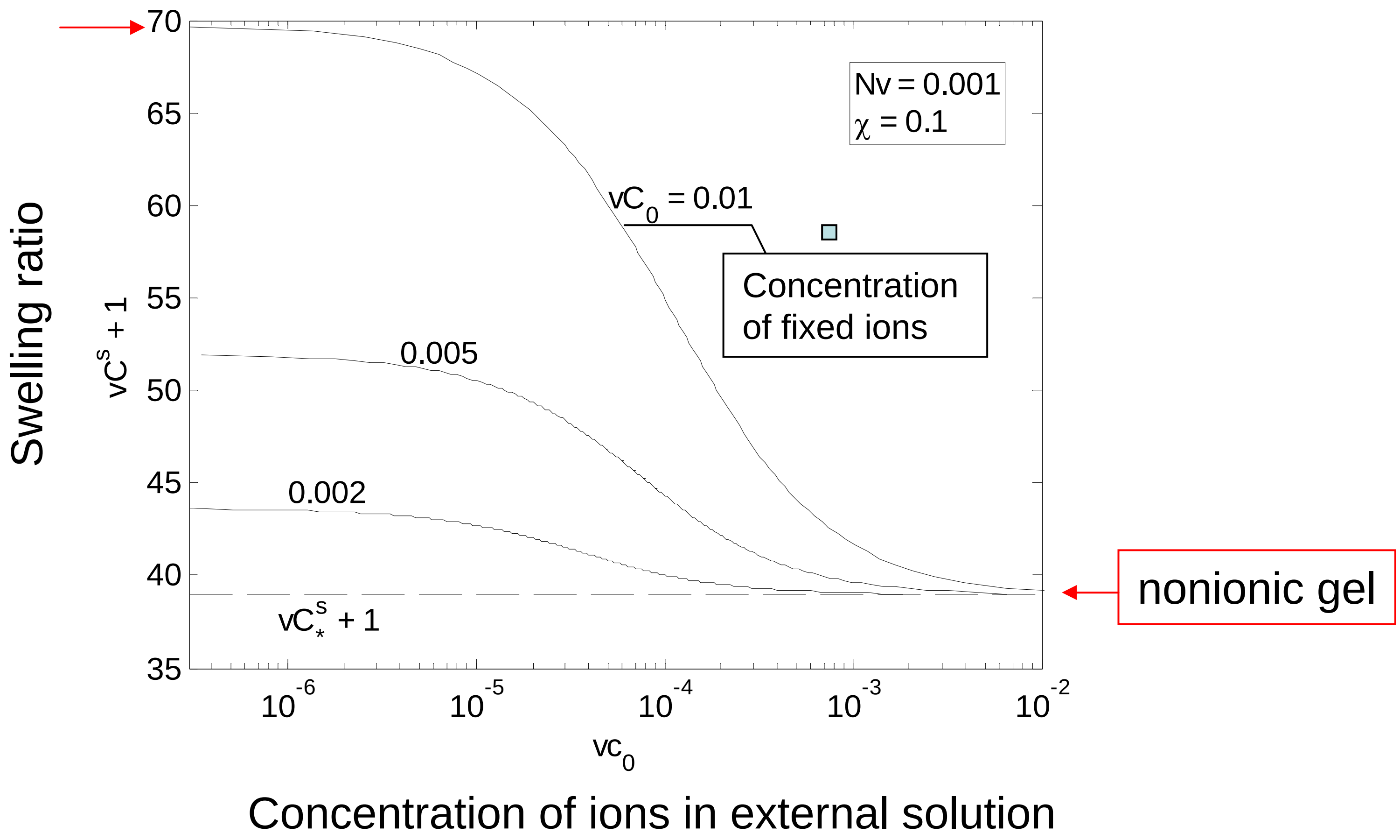
3 ways of doing work to a gel



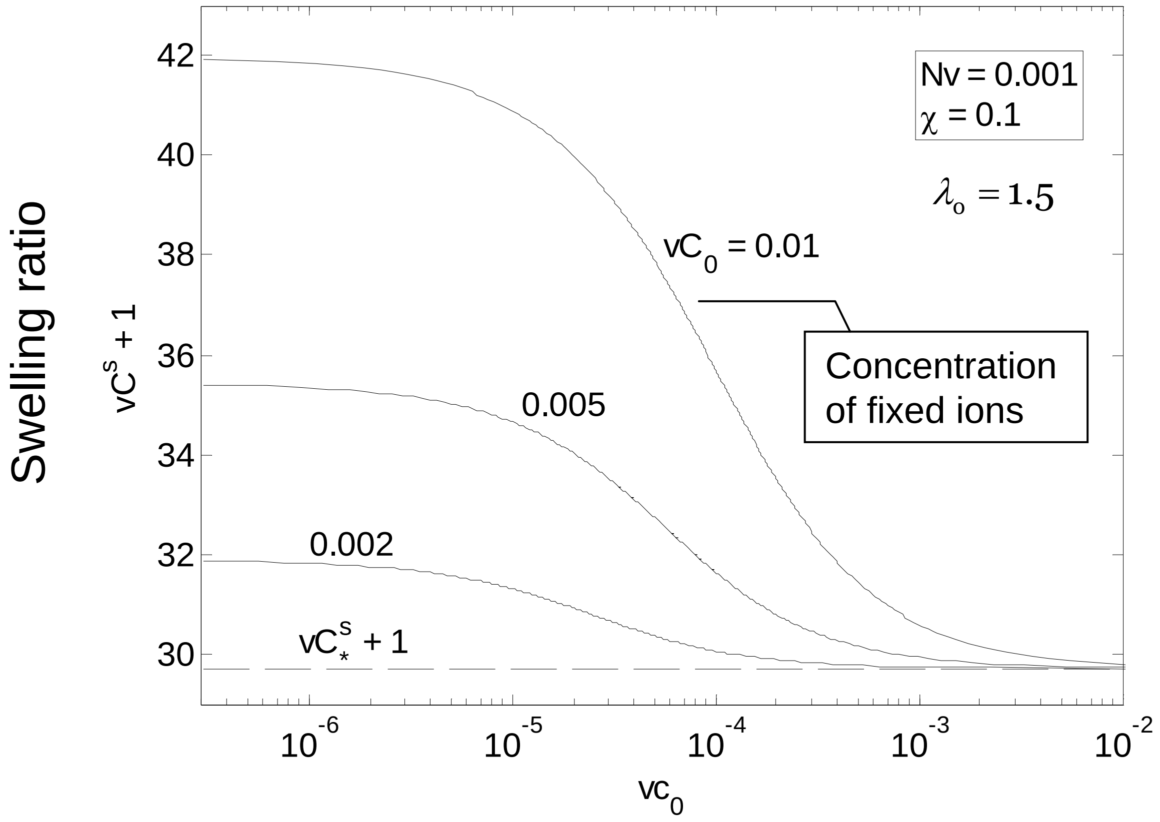
$$\int \delta W dV = \int B_i \delta x_i dV + \int T_i \delta x_i dA + \int \Phi \, \delta q dV + \int \Phi \, \delta \omega dA + \sum_a \mu^a \int \delta C^a dV$$

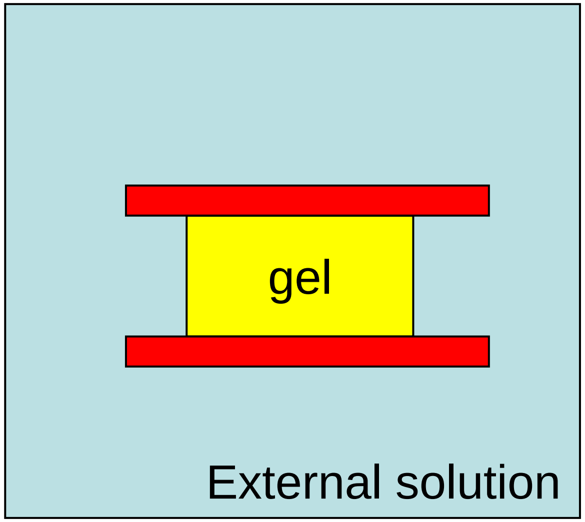
$$W = \frac{\text{free energy of gel}}{\text{volume in reference state}} \qquad C^a(\mathbf{X},t) = \frac{\text{\# of ions of species } a}{\text{volume in reference state}}$$

Swelling regulated by concentration of ions



Constrained swelling

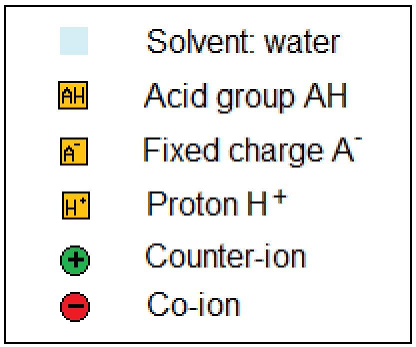


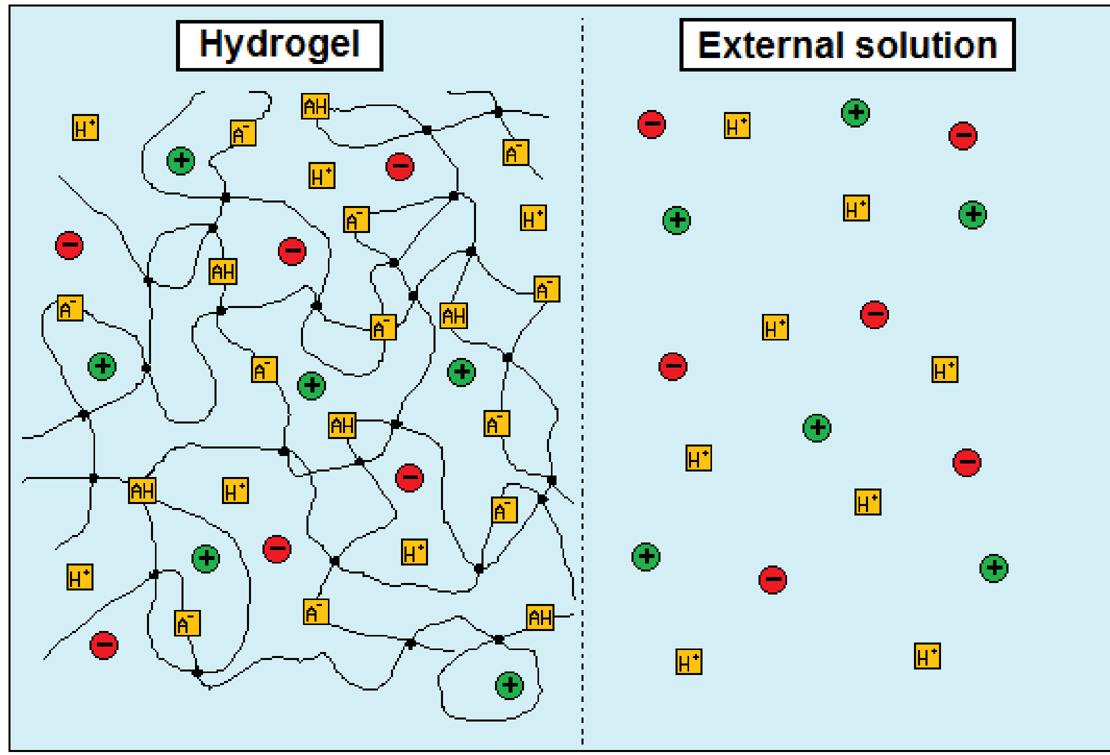


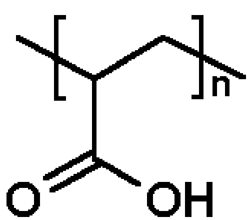
Concentration of ions in external solution

Hong, Zhao, Suo, http://imechanica.org/node/5960

pH-sensitive hydrogel







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

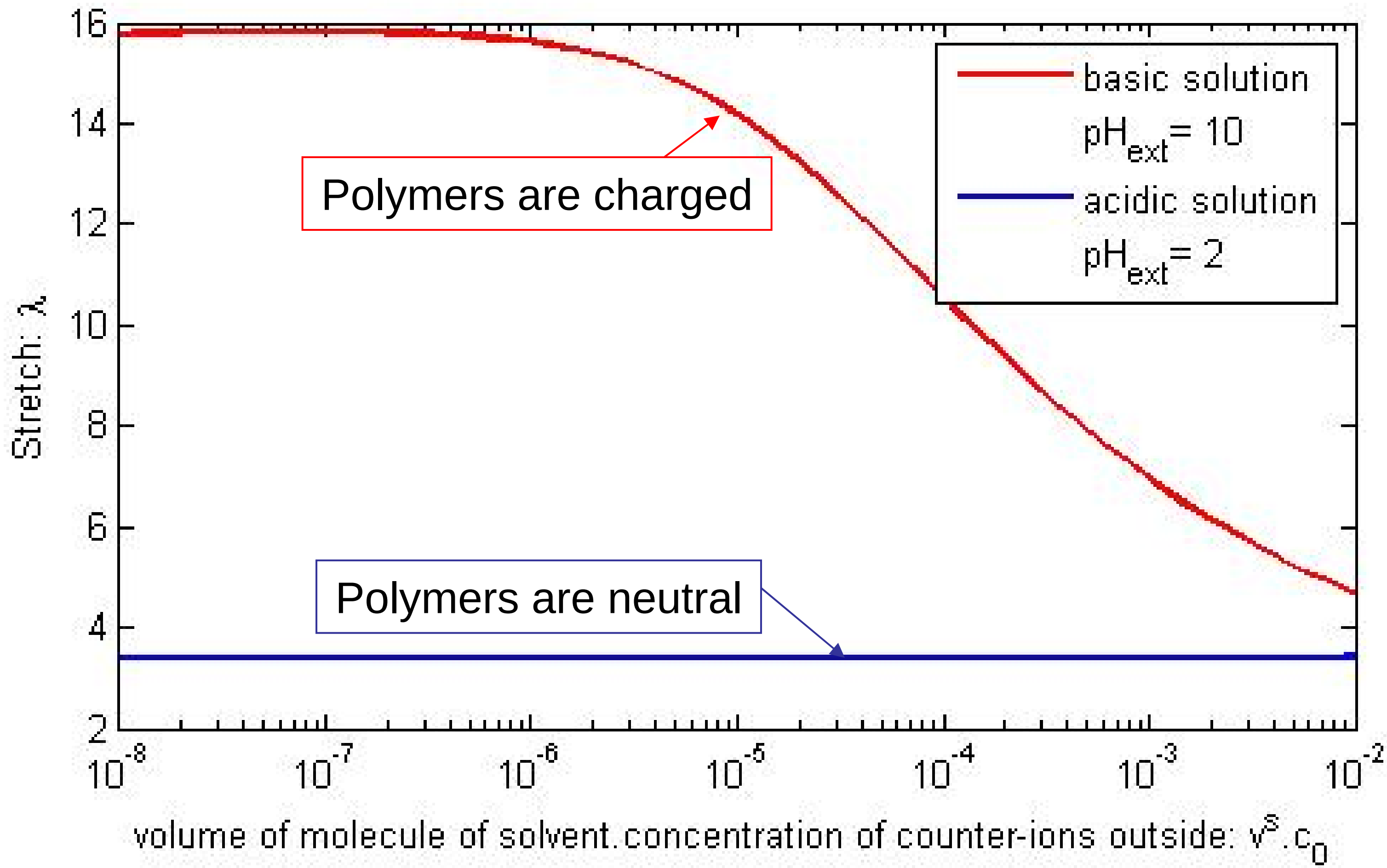
fixed mobile

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

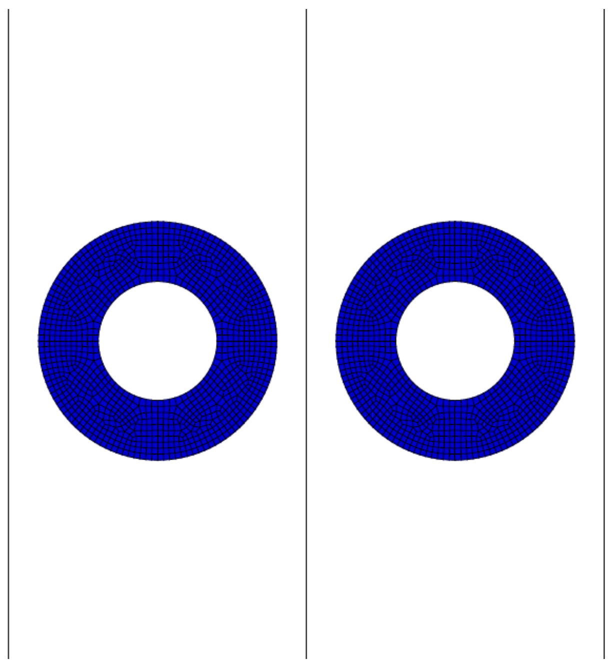
pH-sensitive gel - Free Swelling - influence of pH_{ext}

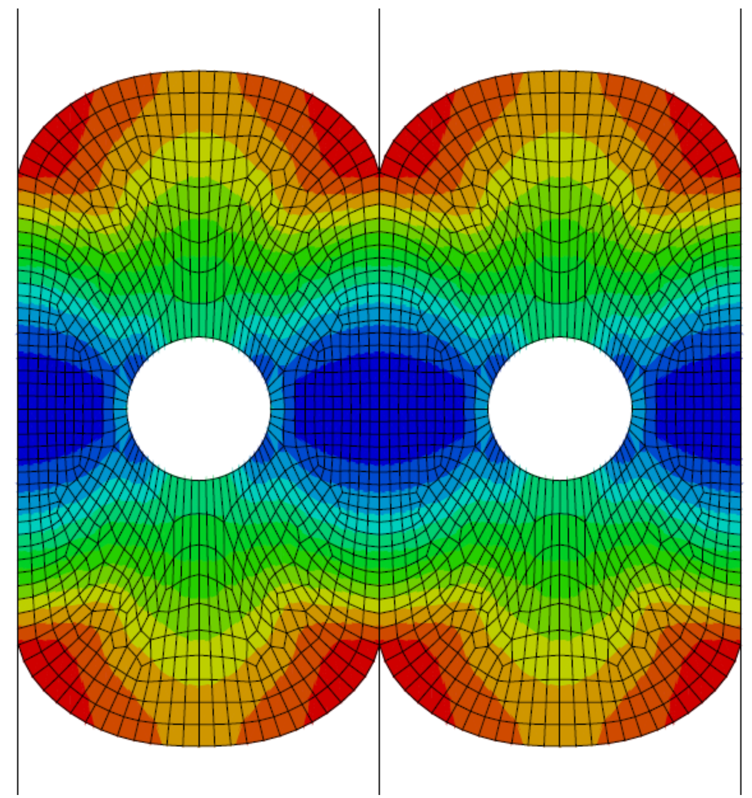
Dimensionless concentration of polymer chains: $N.v^S = 0.001$
Molar fraction of acidic group in polymer: f= 25 %
Flory's interaction parameter: χ= 0.1

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

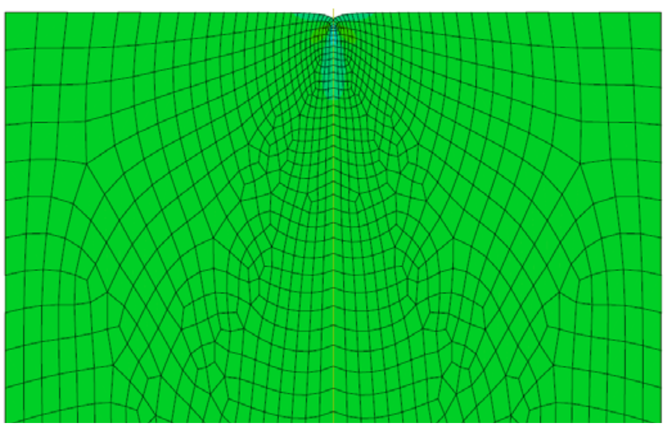


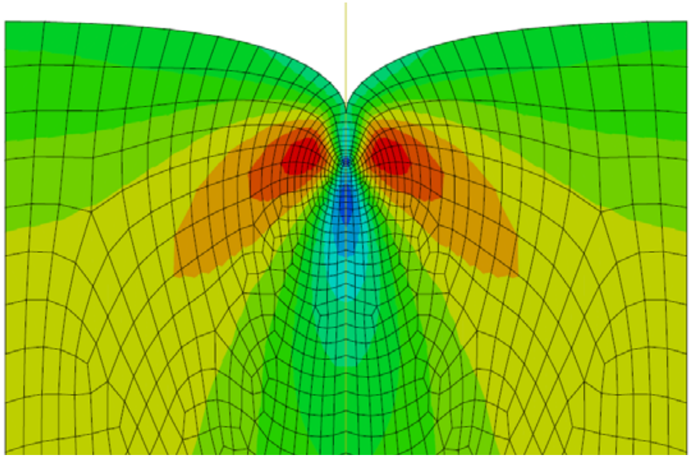
Valve in microfluidics



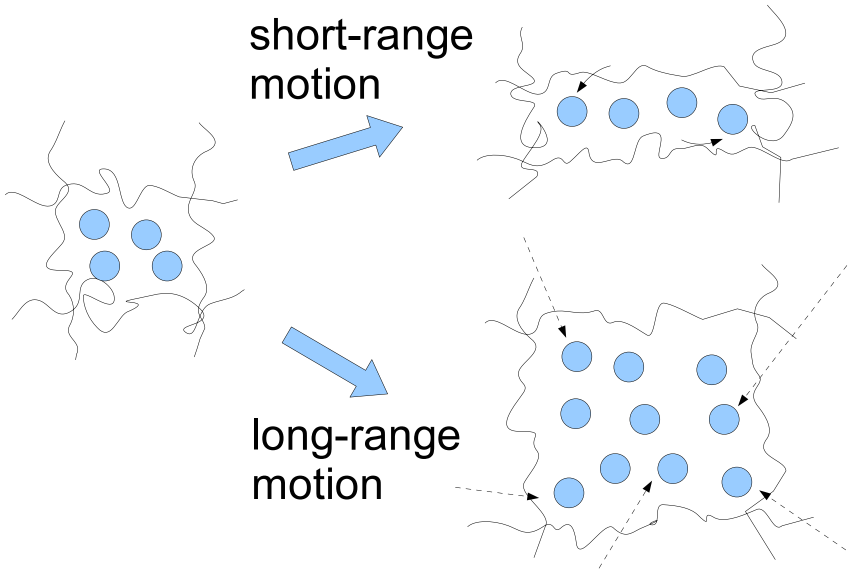


Crease





Time-dependent process

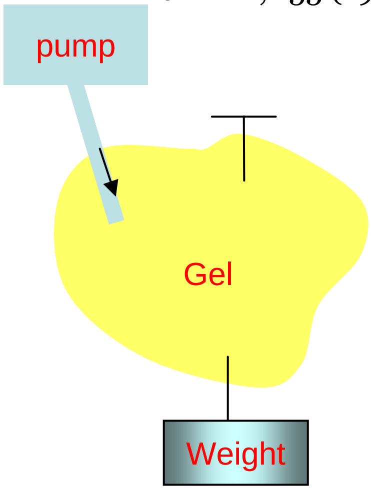


Shape change: short-range motion of solvent molecules, fast
Volume change: long-range motion of solvent molecules, slow

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

Concurrent deformation and migration

Maurice Biot
JAP 12, 155 (1941)



Deformation of network

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

Conservation of solvent

$$\frac{\partial C(\mathbf{X},t)}{\partial t} + \frac{\partial J_K(\mathbf{X},t)}{\partial X_K} = \frac{\partial r(\mathbf{X},t)}{\partial t}$$

$$J_K N_K = -\frac{\partial i(\mathbf{X},t)}{\partial t}$$

Nonequilibrium thermodynamics

$$\int \delta W dV \le \int B_i \delta x_i dV + \int T_i \delta x_i dA + \int \mu \delta r dV + \int \mu \delta i dA$$

Local equilibrium

$$s_{iK} = \frac{\partial W(\mathbf{F},C)}{\partial F_{iK}} \qquad \frac{\partial s_{iK}(\mathbf{X},t)}{\partial X_K} + B_i = 0$$

$$\mu = \frac{\partial W(\mathbf{F},C)}{\partial C} \qquad s_{iK} N_K = T_i$$

Rate process

$$J_K = -M_{KL} \frac{\partial \mu(\mathbf{X},t)}{\partial X_L}$$

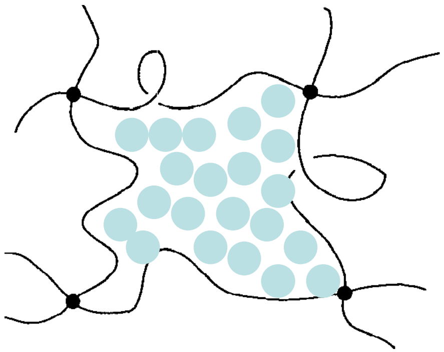
Hong, Zhao, Zhou, Suo, JMPS 56, 1779 (2008)

ideal kinetic model

Solvent molecules migrate in a gel by self-diffusion

$$J_K = -M_{KL} \frac{\partial \mu}{\partial X_L}$$

Diffusion in true quantities $j_i = -\frac{cD}{kT}\frac{\partial \mu}{\partial x_i}$



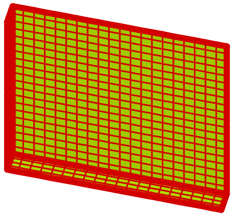
Conversion between true and nominal quantities

$$j_i = \frac{F_{iK}}{\det F} J_K \qquad \frac{\partial \mu}{\partial X_K} = \frac{\partial \mu}{\partial x_i} F_{iK}$$

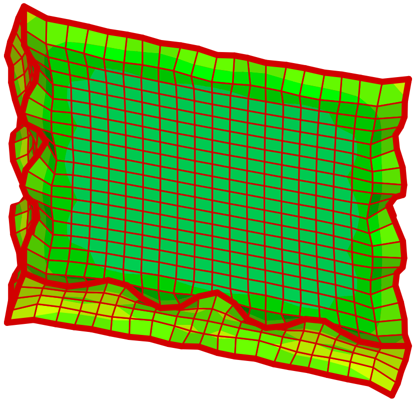
$$M_{KL} = \frac{D}{\upsilon kT} H_{iK} H_{iL} \left(\det F - 1\right)$$

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

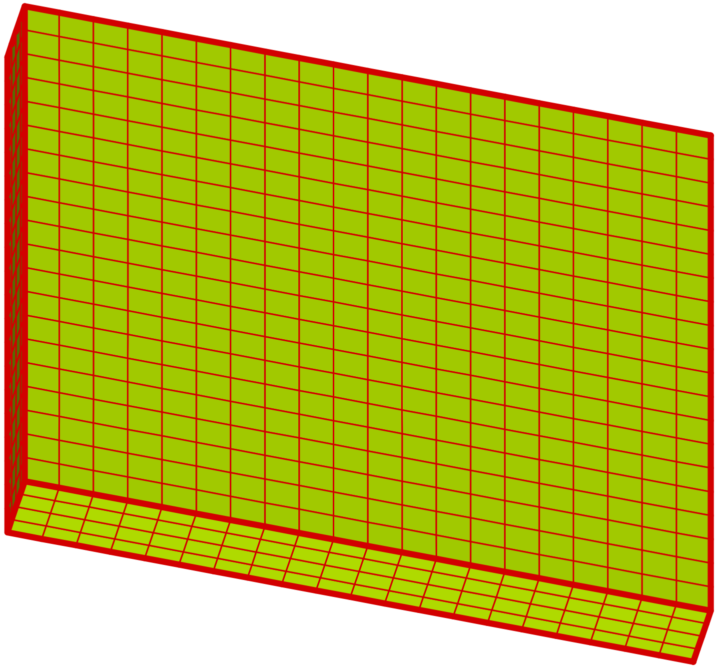
Finite element method for concurrent deformation and migration



$Dt/L^2 = 0$



$Dt/L^2 = 10$

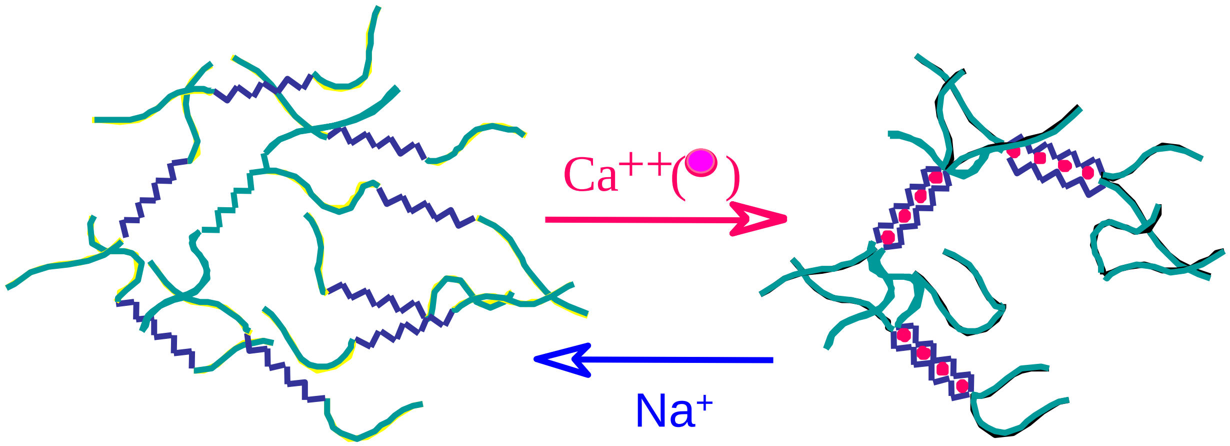


$Dt/L^2 = \infty$

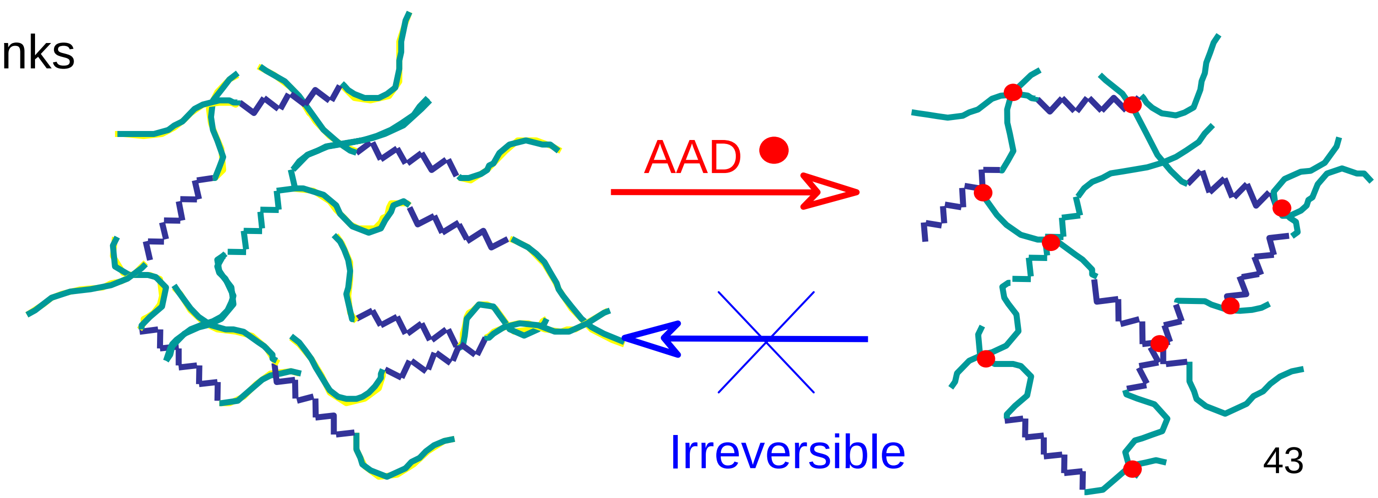
Zhang, Zhao, Suo, Jiang, JAP 105, 093522 (2009)

Alginate Hydrogels

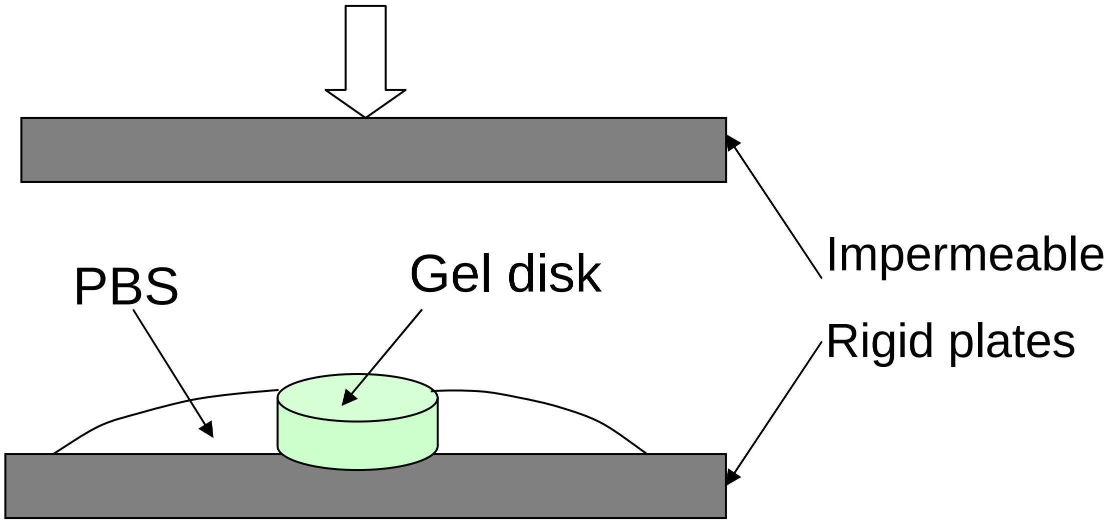
Ionic crosslinks

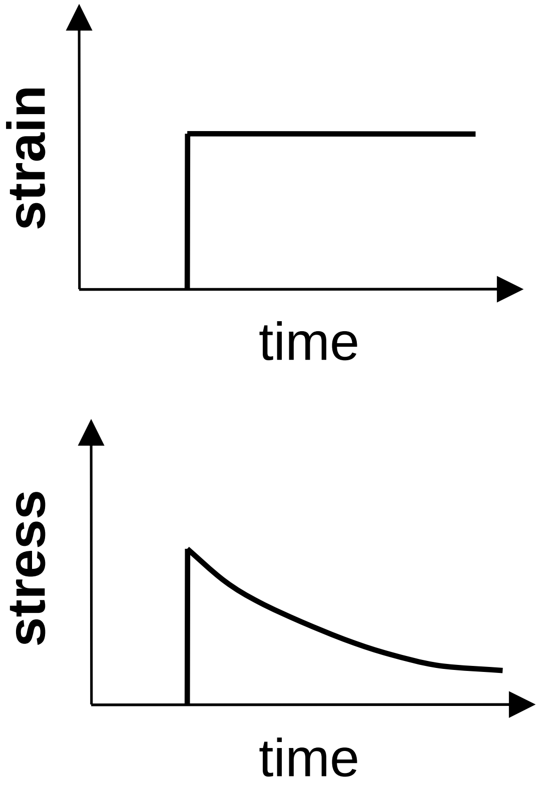


Covalent crosslinks



Stress-relaxation test

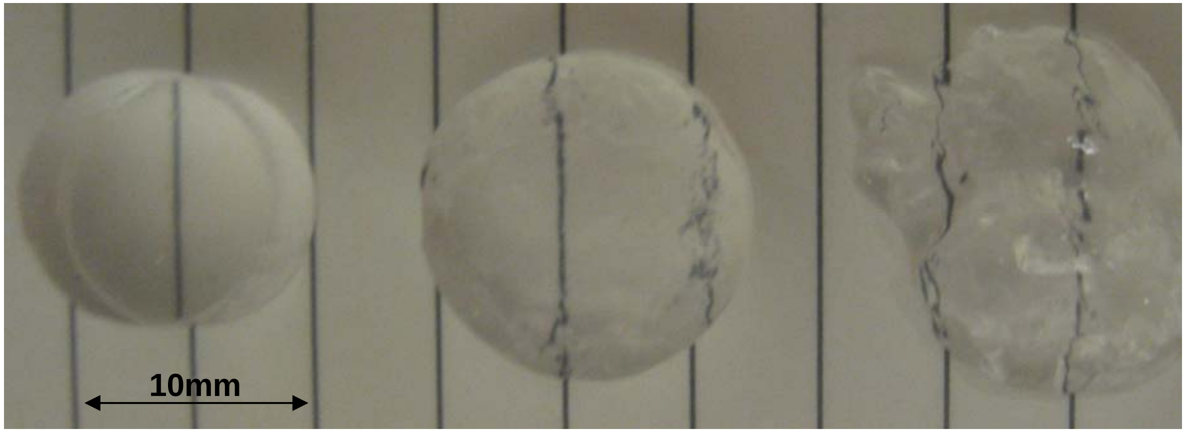




Zhao, Huebsch, Mooney, Suo, submitted.

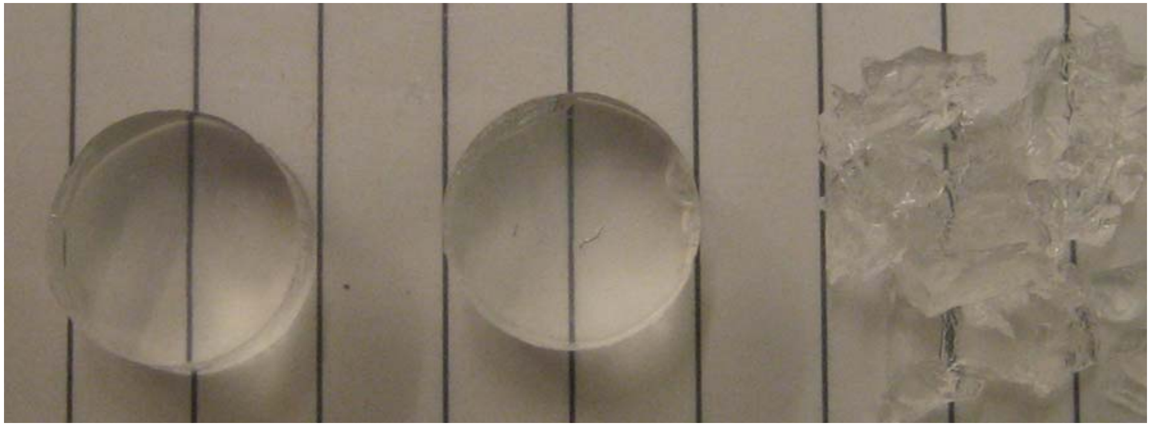
Elasticity, plasticity, fracture

Ionic crosslinks



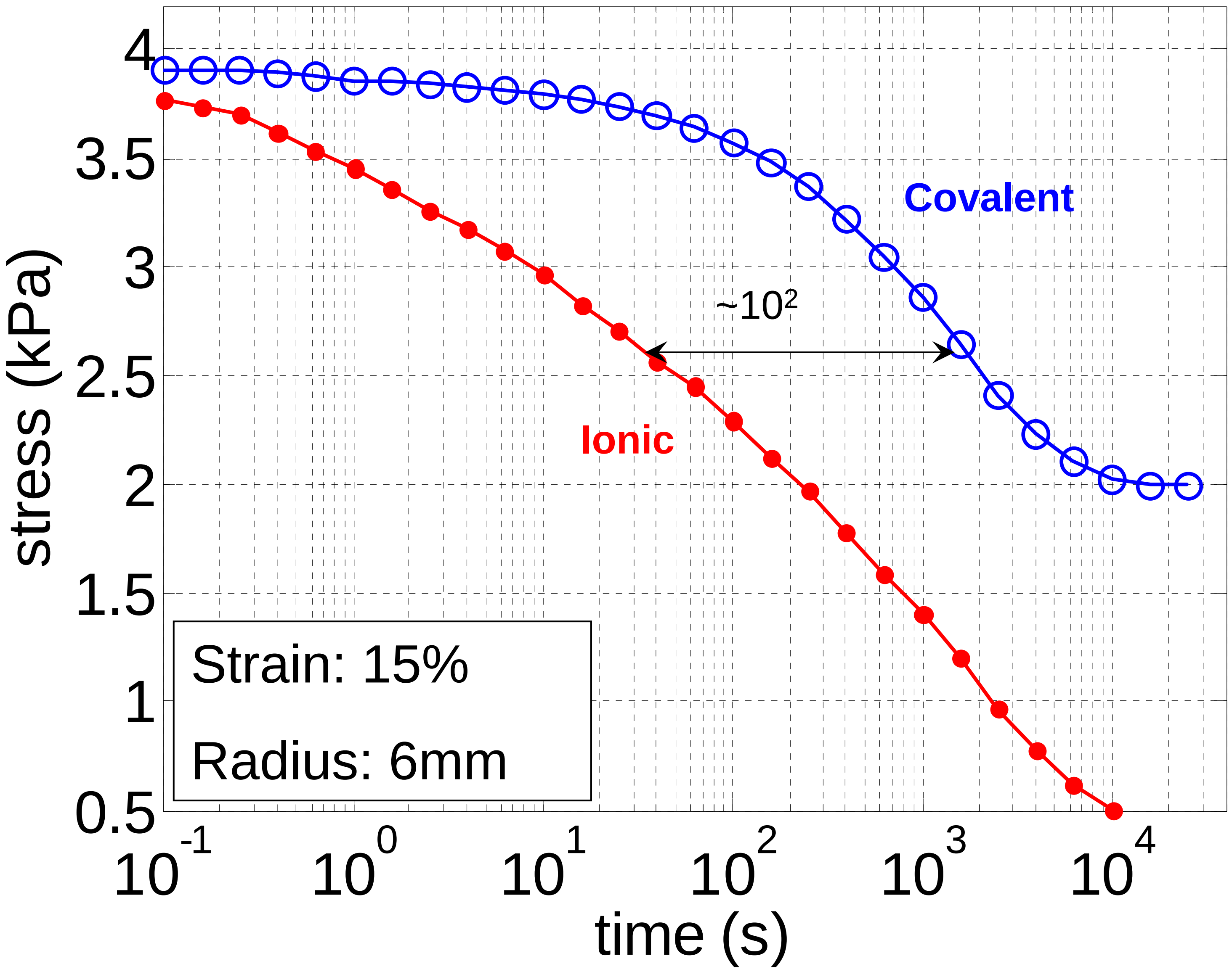
Swollen state **45% compressive strain** **50% compressive strain**

Covalent crosslinks

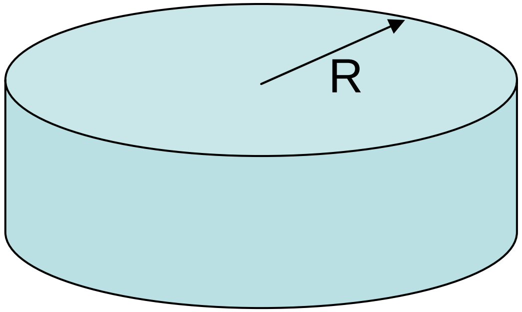


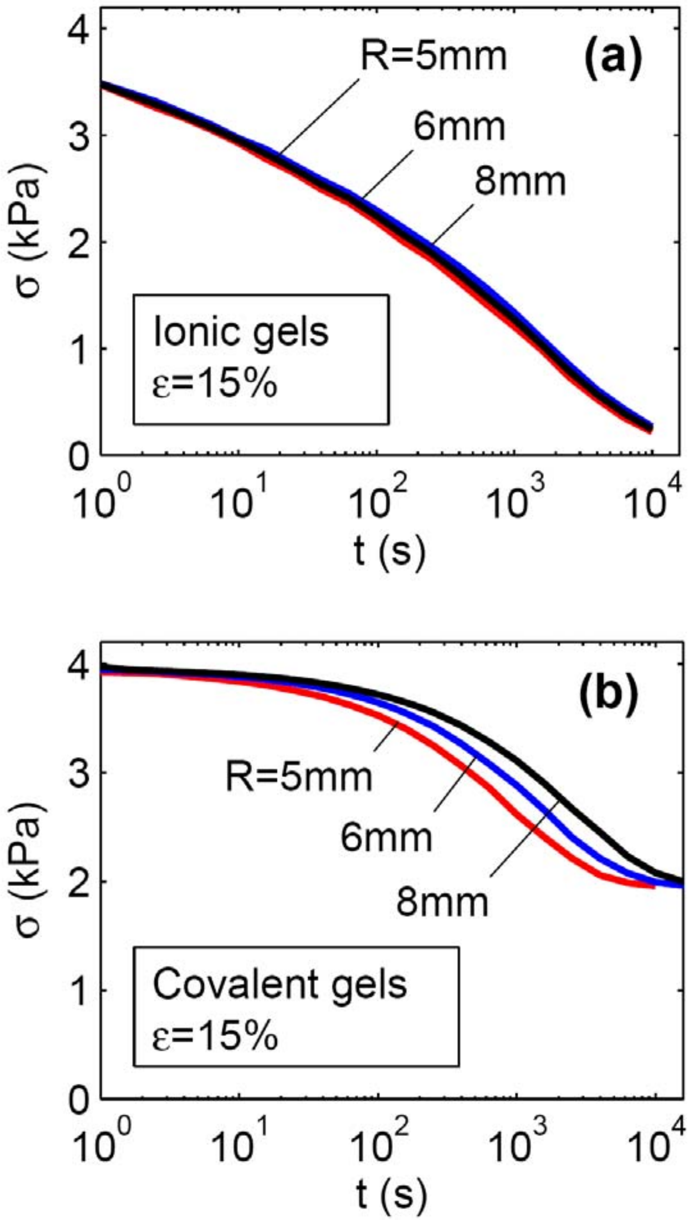
Swollen state **15% compressive strain** **20% compressive strain**

Stress Relaxation

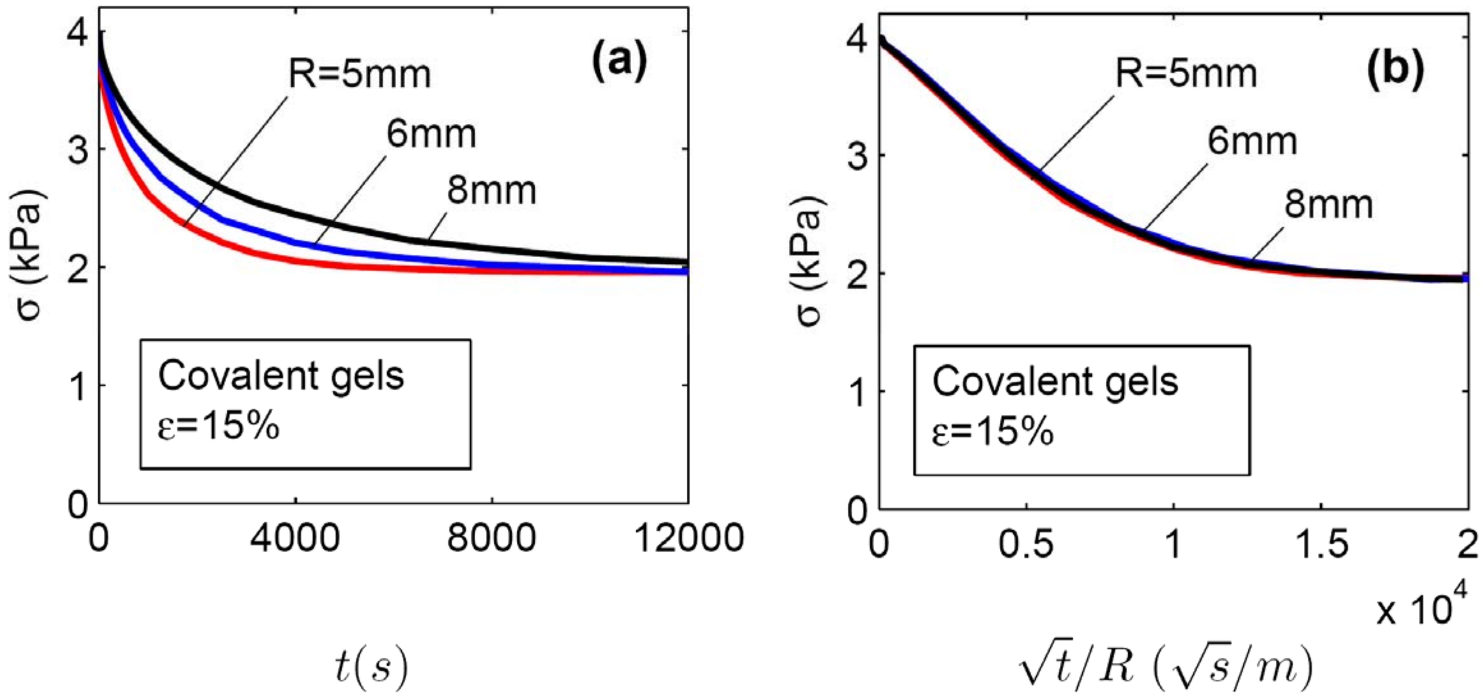


Size effect


R


(a)
R=5mm
6mm
8mm
Ionic gels
ε=15%
σ (kPa)
t (s)
(b)
R=5mm
6mm
8mm
Covalent gels
ε=15%
σ (kPa)
t (s)

Gel with covalent crosslinks relaxes stress by migration of water



$$\sigma(t,R) = f\left(\frac{\sqrt{t}}{R}\right)$$

$$D \sim \frac{R^2}{t_{relax}} \sim 10^{-8}\, \mathrm{m}^2/\mathrm{s}$$

Outlook

- Soft Active Materials (SAMs) have many uses (microfluidics, artificial muscles, drug delivery, tissue engineering, water treatment, packers in oil wells).
- Mechanics of SAMs is interesting and challenging (large deformation, mass transport, multiple thermodynamic forces, many modes of instability).
- The field is wide open (fabrication, computation, devices, phenomena).

3 lectures on SAMs: http://imechanica.org/node/3215

•Dielectric elastomers

•Gels

•Polyelectrolytes