Large deformation and instability in swelling polymeric gels

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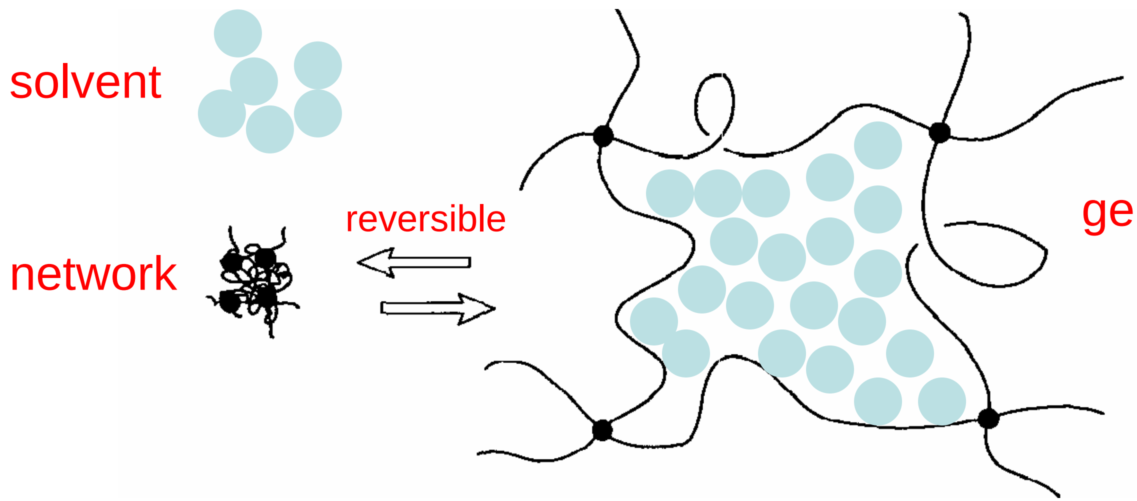
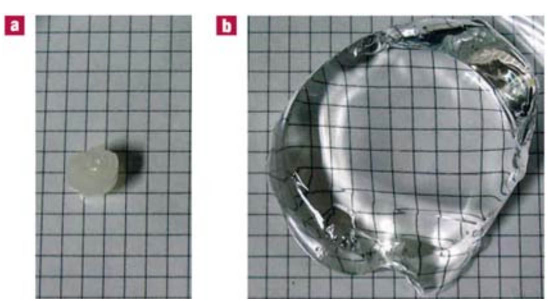
gel = network + solvent



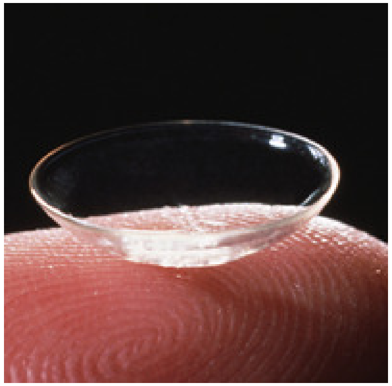
Solid-like: long polymers crosslink by strong bonds. Retain shape
Liquid like: polymers and solvent aggregate by weak bonds. Enable transport



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

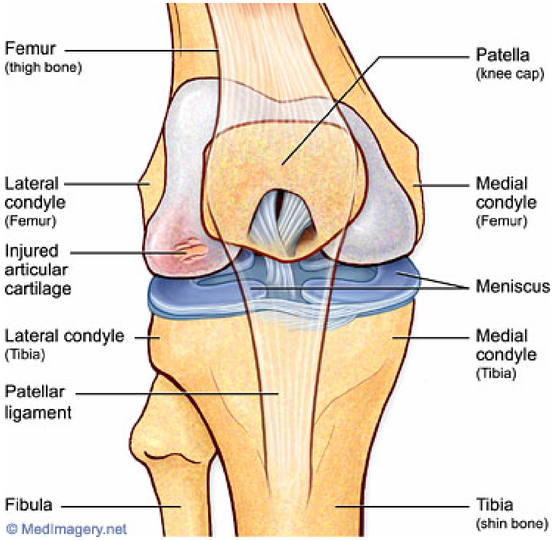
Gels in daily life

food

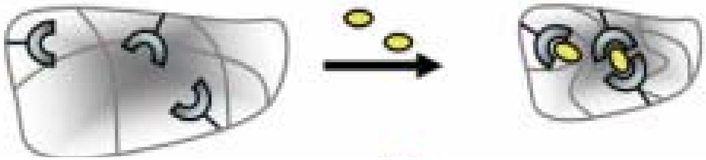


Contact lenses

Wichterie, Lim, Nature 185, 117 (1960)



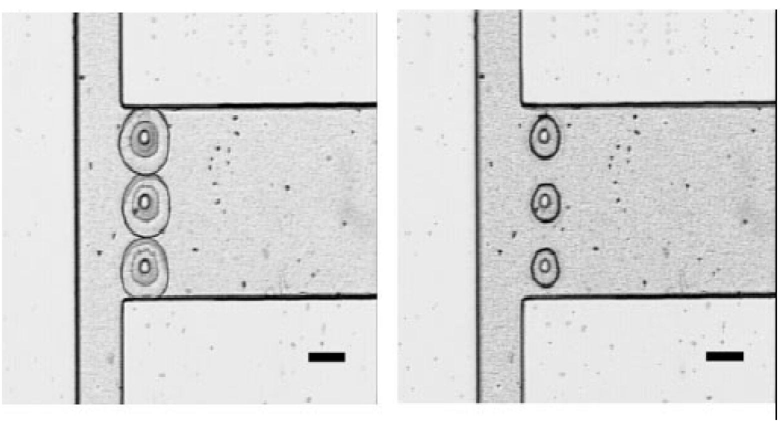
Tissues, natural or engineered



Drug delivery

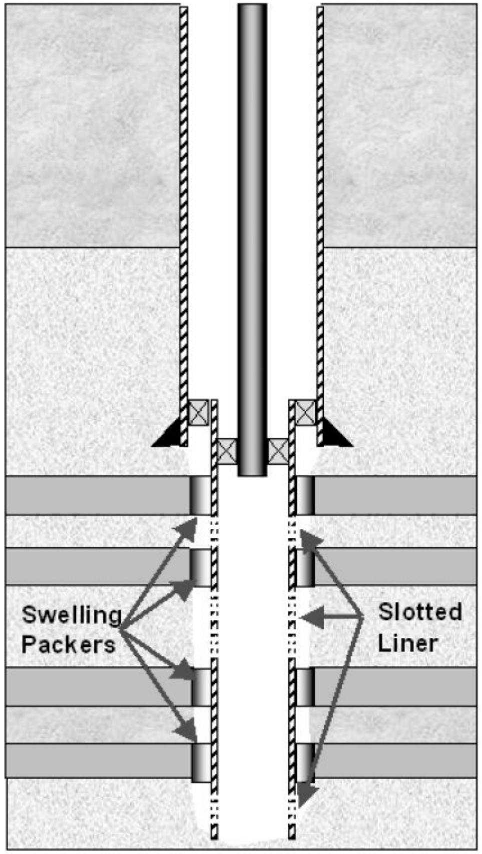
Ulijn et al. Materials Today 10, 40 (2007)

Gels in engineering



Valve in fluidics

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



packer in oil well

Shell, 2003

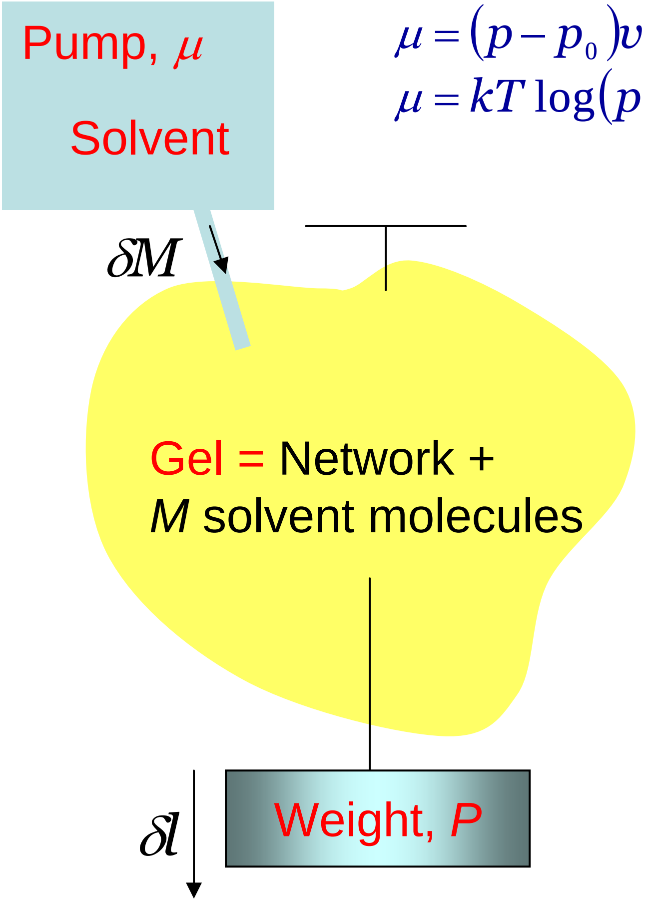
Two ways of doing work to a gel

$\mu \delta M$ work done by the pump

$P \delta l$ work done by the weight

$F(l, M)$ Helmholtz free energy of gel

$$\mu = (p - p_0)v$$
$$\mu = kT \log(p / p_0)$$



Equilibrium condition

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

$$P = \frac{\partial F(l, M)}{\partial l} \qquad \mu = \frac{\partial F(l, M)}{\partial M}$$

Field variables

Equilibrium condition

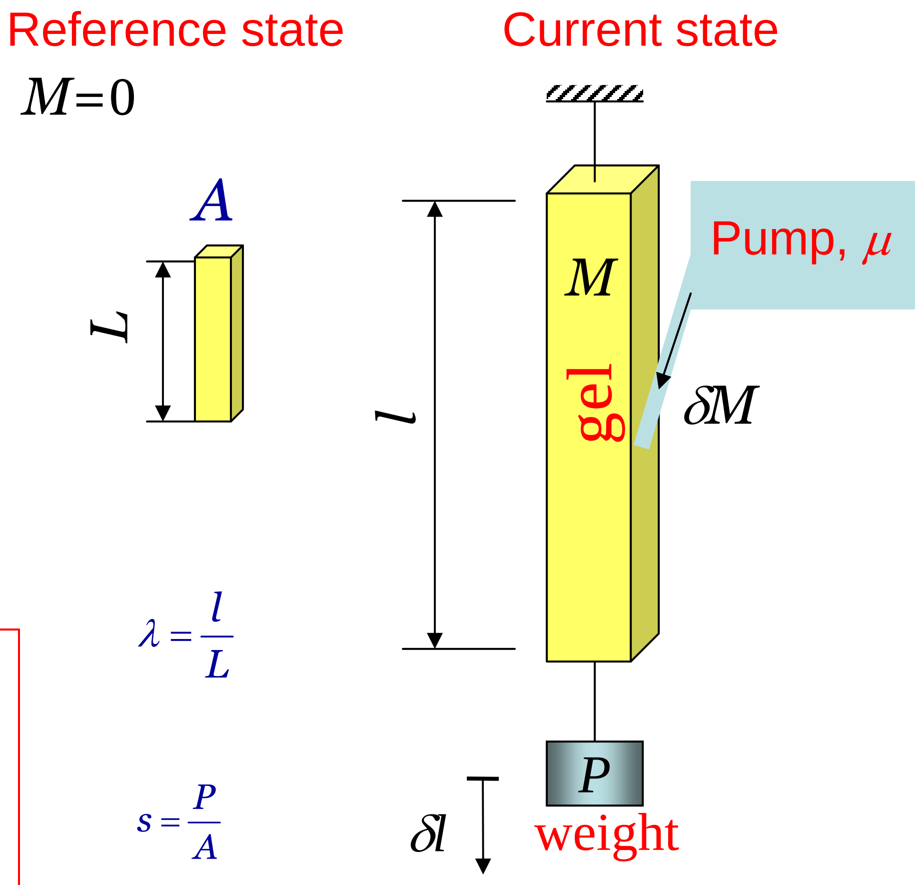
$$\delta F = P\delta l + \mu \delta M$$

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

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

$$s = \frac{\partial W(\lambda, C)}{\partial \lambda} \qquad \mu = \frac{\partial W(\lambda, C)}{\partial C}$$

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



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

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

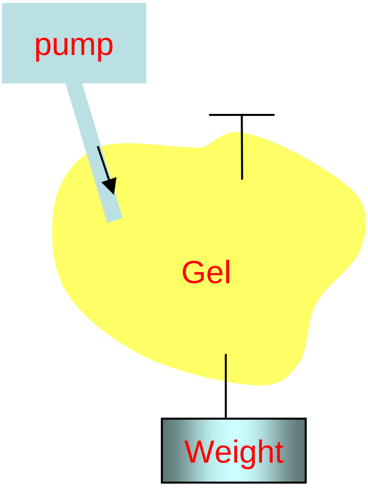
$$C = \frac{M}{AL}$$

3D inhomogeneous field

Deformation gradient	Concentration	Free-energy function
$F_{iK} = \dfrac{\partial x_i(\mathbf{X},t)}{\partial X_K}$	$C(\mathbf{X},t)$	$W(\mathbf{F},C)$

Equilibrium condition

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



Equivalent equilibrium condition

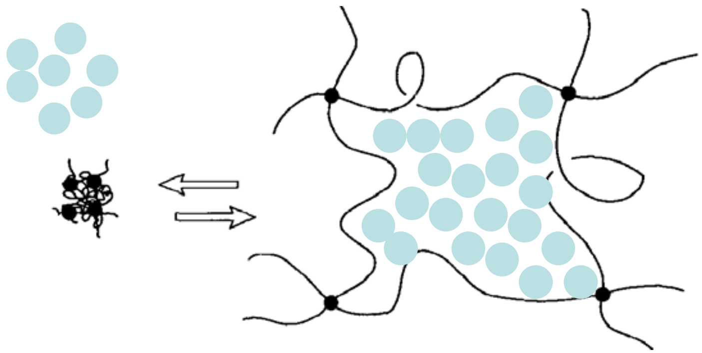
$$s_{iK} = \frac{\partial W(\mathbf{F},C)}{\partial F_{iK}} \qquad \mu = \frac{\partial W(\mathbf{F},C)}{\partial C}$$

$$\frac{\partial s_{iK}}{\partial X_K} + B_i = 0 \qquad s_{iK} N_K = T_i$$

Gibbs (1878)

Flory-Rehner free energy

Swelling increases entropy by mixing solvent and polymers, but decreases entropy by straightening polymers.



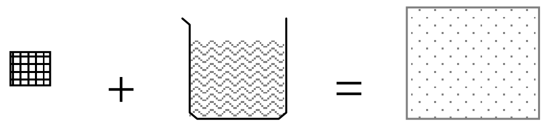
Free-energy function $$W(\mathbf{F},C)=W_s(\mathbf{F})+W_m(C)$$

Free energy of stretching $$W_s(\mathbf{F})=\tfrac{1}{2}NkT\left[F_{iK}F_{iK}-3-2\log(\det\mathbf{F})\right]$$

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

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

Molecular incompressibility



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

$$1 + \upsilon C = \det \mathbf{F}$$

υ – volume per solvent molecule

Assumptions:

- Individual solvent molecule and polymer are incompressible.
- Neglect volumetric change due to physical association
- Gel has no voids. (a gel is different from a sponge.)

Equations of state

Enforce molecular incompressibility as a constraint by introducing a Lagrange multiplier Π

$$\hat{W} = W(\mathbf{F}, C) + \Pi(1 + vC - \det \mathbf{F})$$

Equations of state

$$s_{iK} = \frac{\partial W(\mathbf{F}, C)}{\partial F_{iK}} - \Pi H_{iK} \det \mathbf{F} \qquad \mu = \frac{\partial W(\mathbf{F}, C)}{\partial C} + \Pi v$$

Use the Flory-Rehner free energy

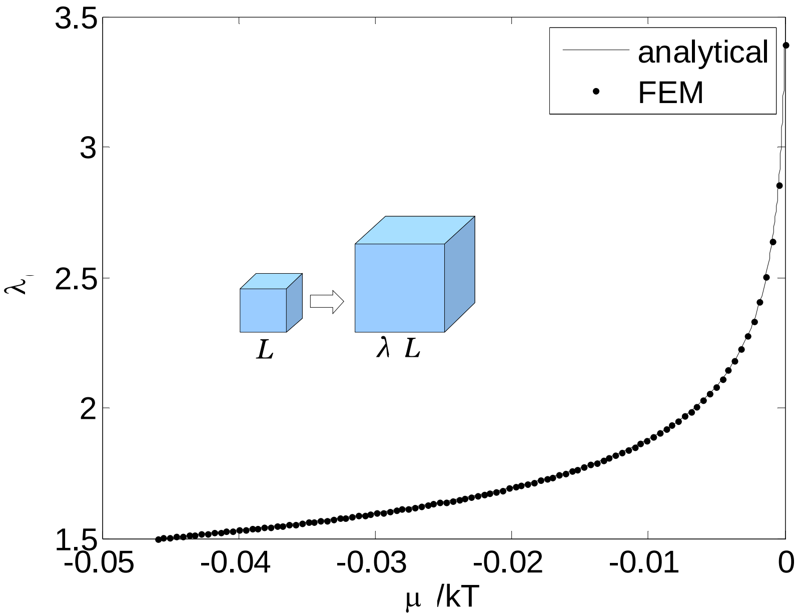
$$s_{iK} = NkT(F_{iK} - H_{iK}) - \Pi H_{iK} \det \mathbf{F} \qquad \mu = kT\left[\log \frac{vC}{1+vC} + \frac{1}{1+vC} + \frac{\chi}{(1+vC)^2}\right] + \Pi v$$

$$s_1 = NkT(\lambda_1 - \lambda_1^{-1}) - \Pi \lambda_2 \lambda_3 \qquad s_2 = NkT(\lambda_2 - \lambda_2^{-1}) - \Pi \lambda_3 \lambda_1 \qquad s_3 = NkT(\lambda_3 - \lambda_3^{-1}) - \Pi \lambda_1 \lambda_2$$

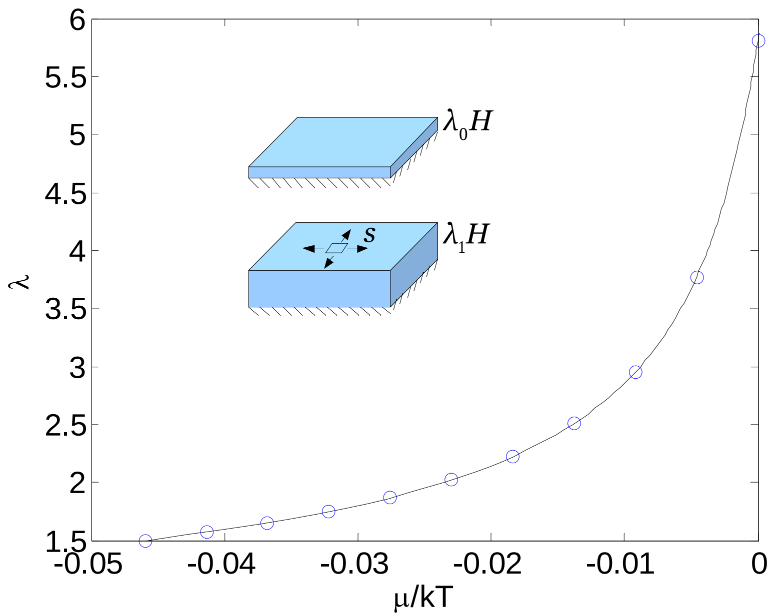
Hong, Zhao, Zhou, Suo, JMPS 56, 1779 (2008)

Anisotropic swelling

Free swelling



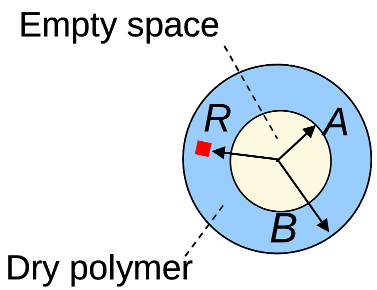
Unidirectional swelling



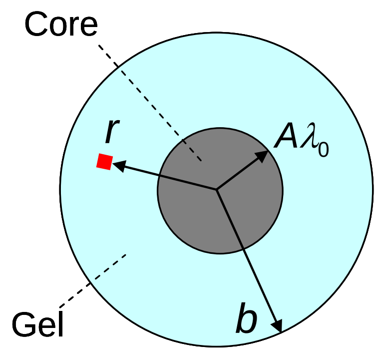
A gel imbibes different amount of solvent under constraint.

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

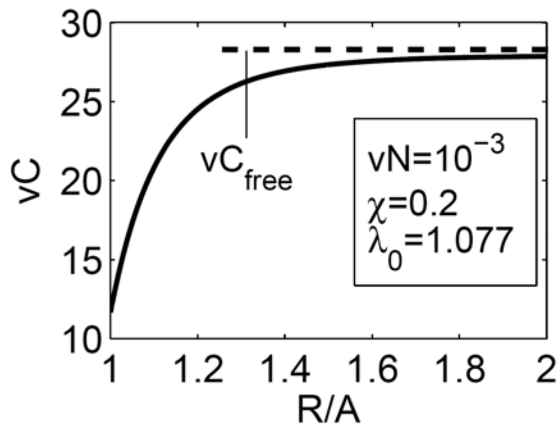
Inhomogeneous swelling

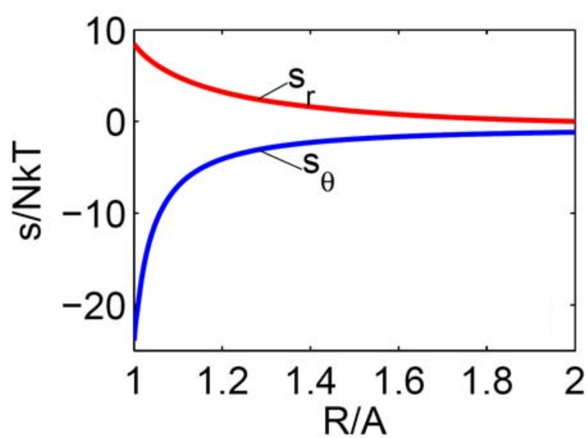


Reference State



Equilibrium State

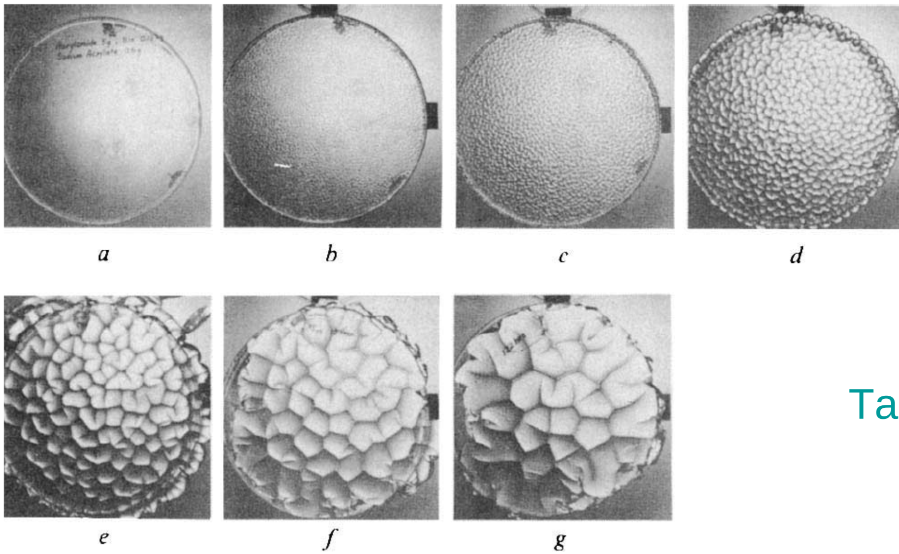




- Concentration is inhomogeneous even in equilibrium.
- Stress is high near the interface (debond, cavitation, crease).

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

Crease



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

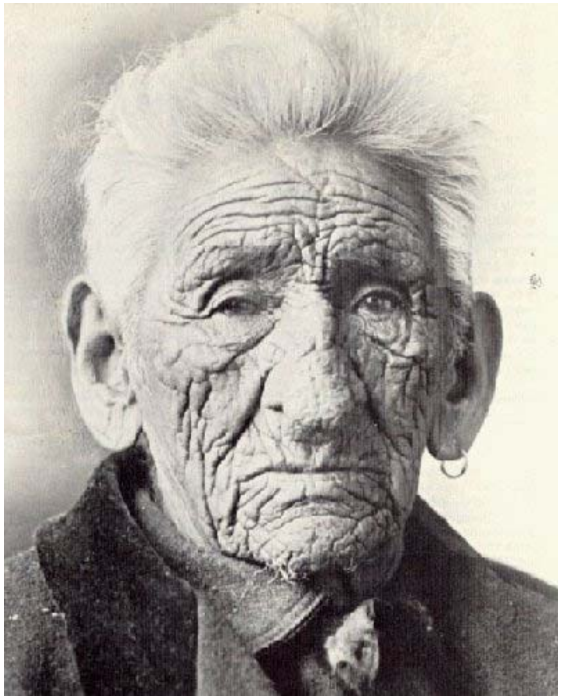
Denian

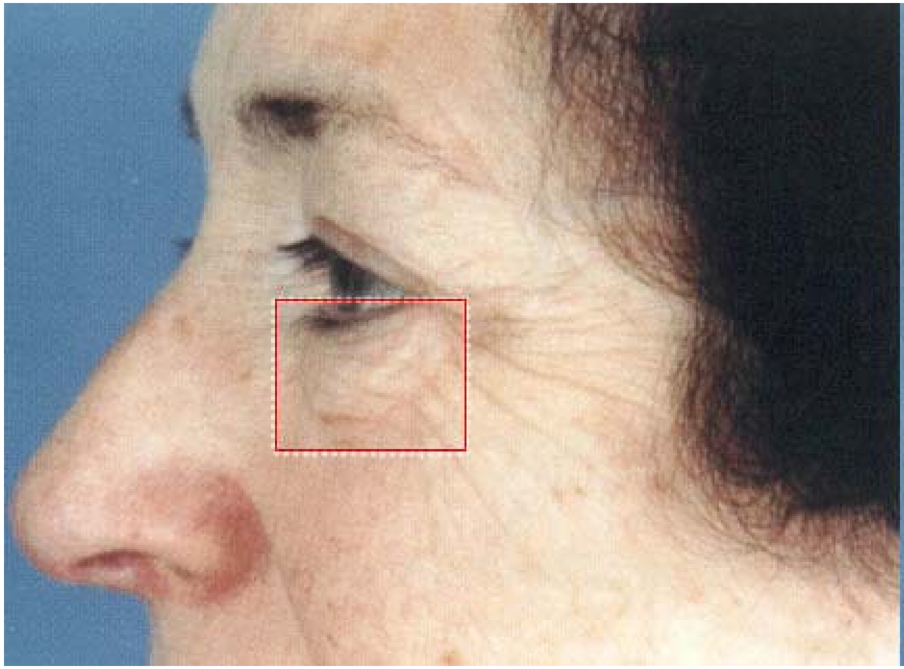
Rising bread dough

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.

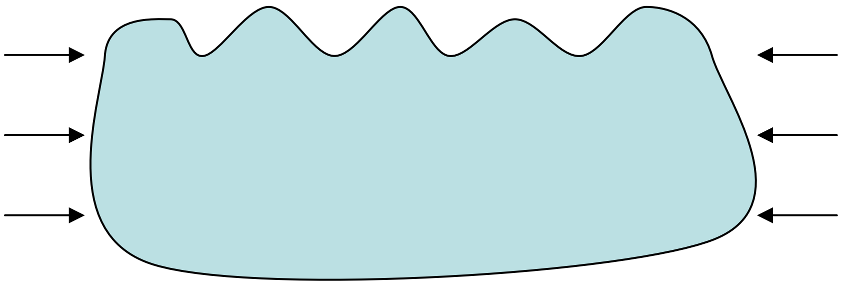
-- An email from **Michael Thouless**

The brain



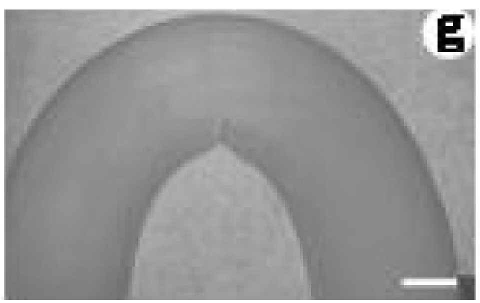


The science of crease: a linearized history



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

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



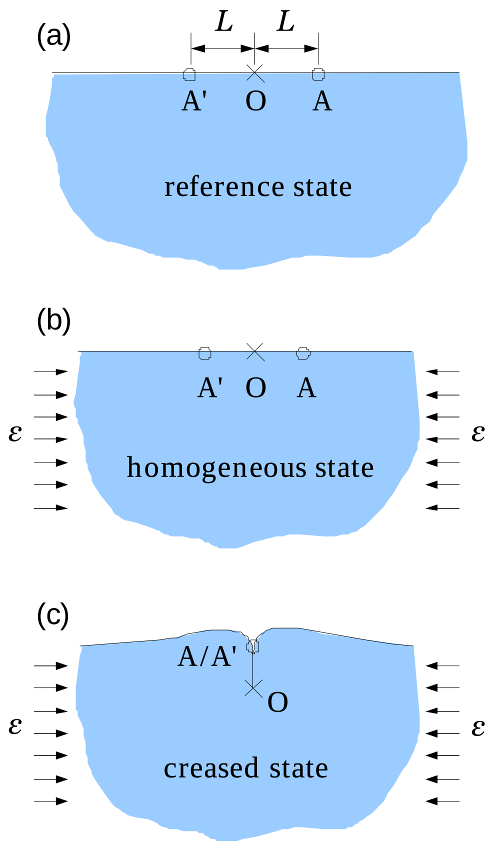
Gent, Cho, Rubber Chemistry and Technology 72, 253 (1999)
Ghatak, Das, PRL 99, 076101 (2007)
Experiments: bending rods of rubber and gels

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

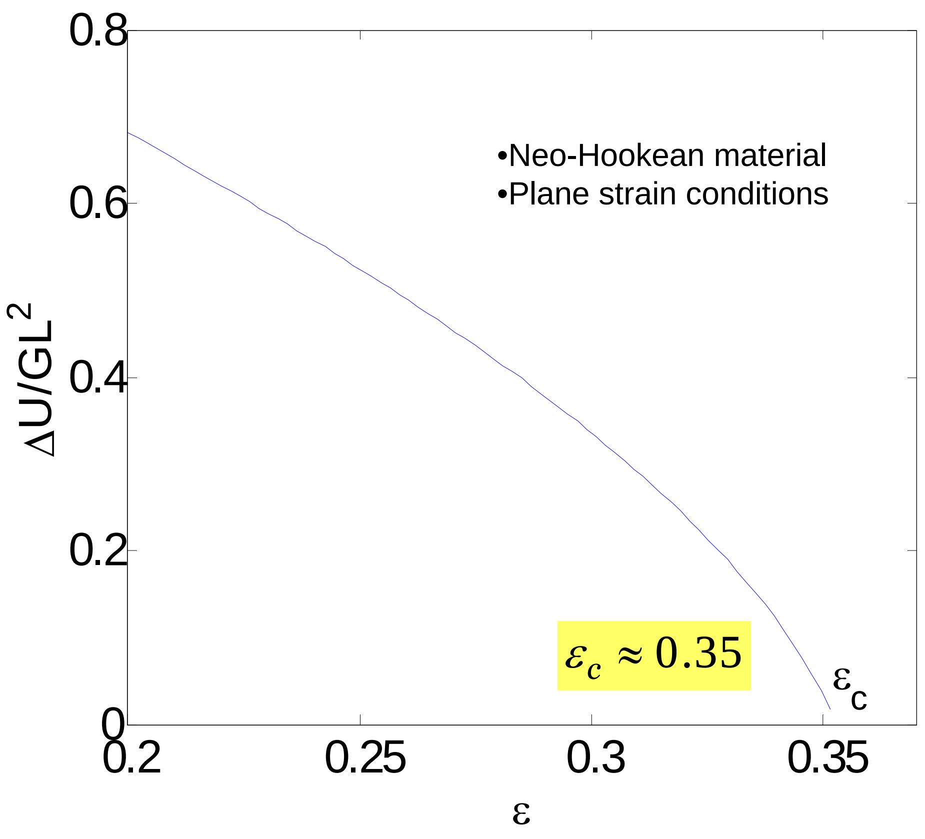
Hohlfeld, Mahadevan, manuscript in preparation (2008)
A new theory: crease is a distinct instability different from that analyzed by Biot.

Hong, Zhao, Suo, manuscript in preparation (2008)
Crease under various conditions.

An energetic model

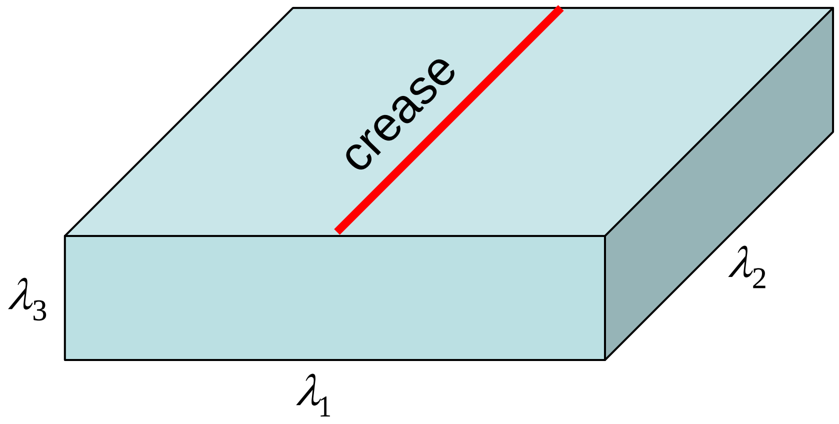


$$\boxed{\Delta U = L^2 G f(\varepsilon)}$$



Hong, Zhao, Suo, manuscript in preparation

Crease under general loading



Incompressibility

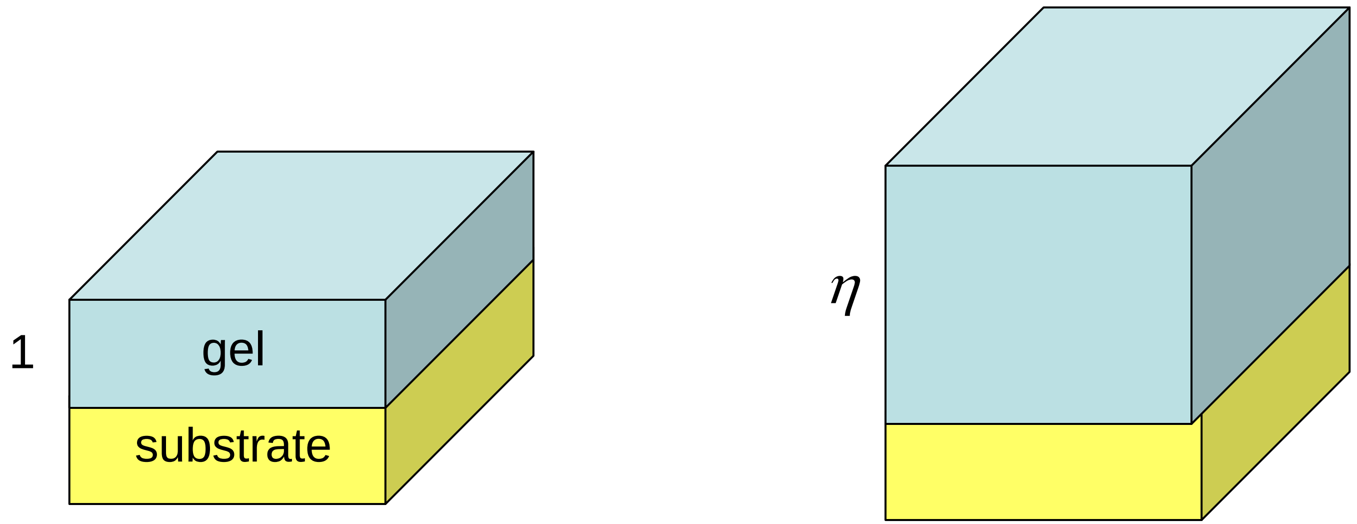
$$\lambda_1\lambda_2\lambda_3 = 1$$

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

Biot $\lambda_3 / \lambda_1 = 3.4$

Hong, Zhao, Suo, manuscript in preparation

Crease of a swelling gel



Theories

$$\eta_c = 2.4$$

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

Experimental data

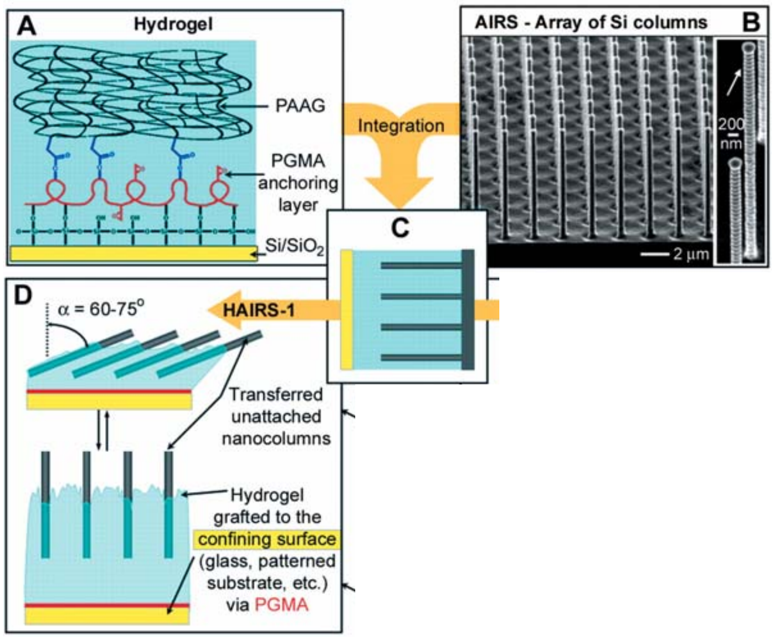
Southern, Thomas, J. Polym. Sci., Part A, 3, 641 (1965) $\eta_{\exp} = 2.4$

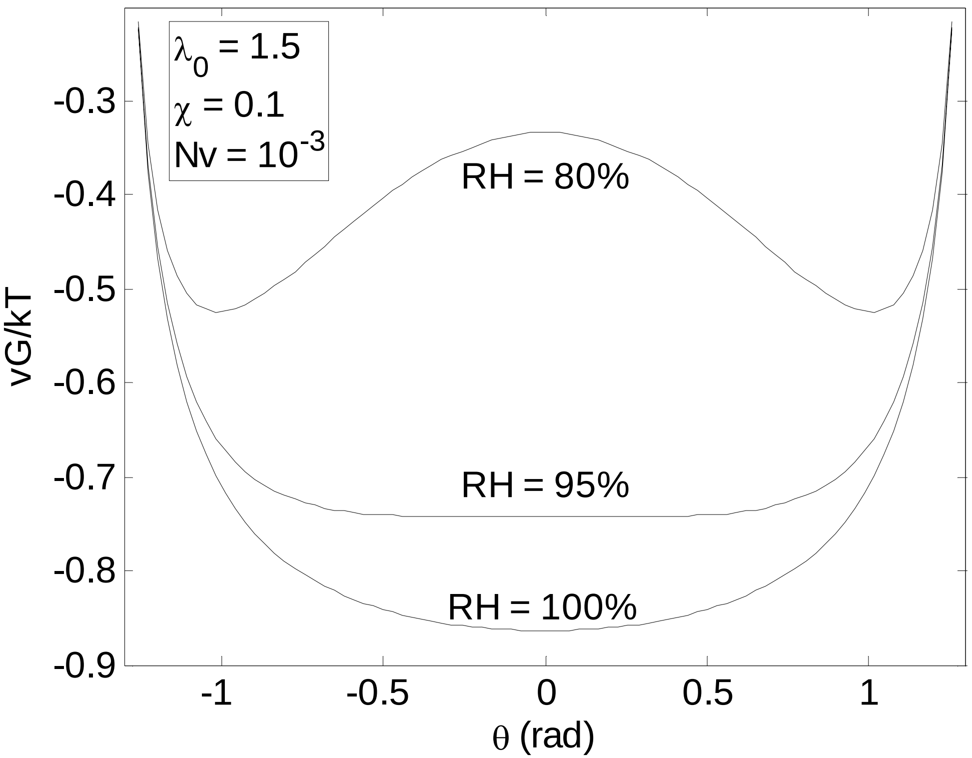
Tanaka, PRL 68, 2794 (1992) $\eta_{\exp} = 2.5 - 3.7$

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

Hong, Zhao, Suo, manuscript in preparation

Hydrogel-actuated nanostructure

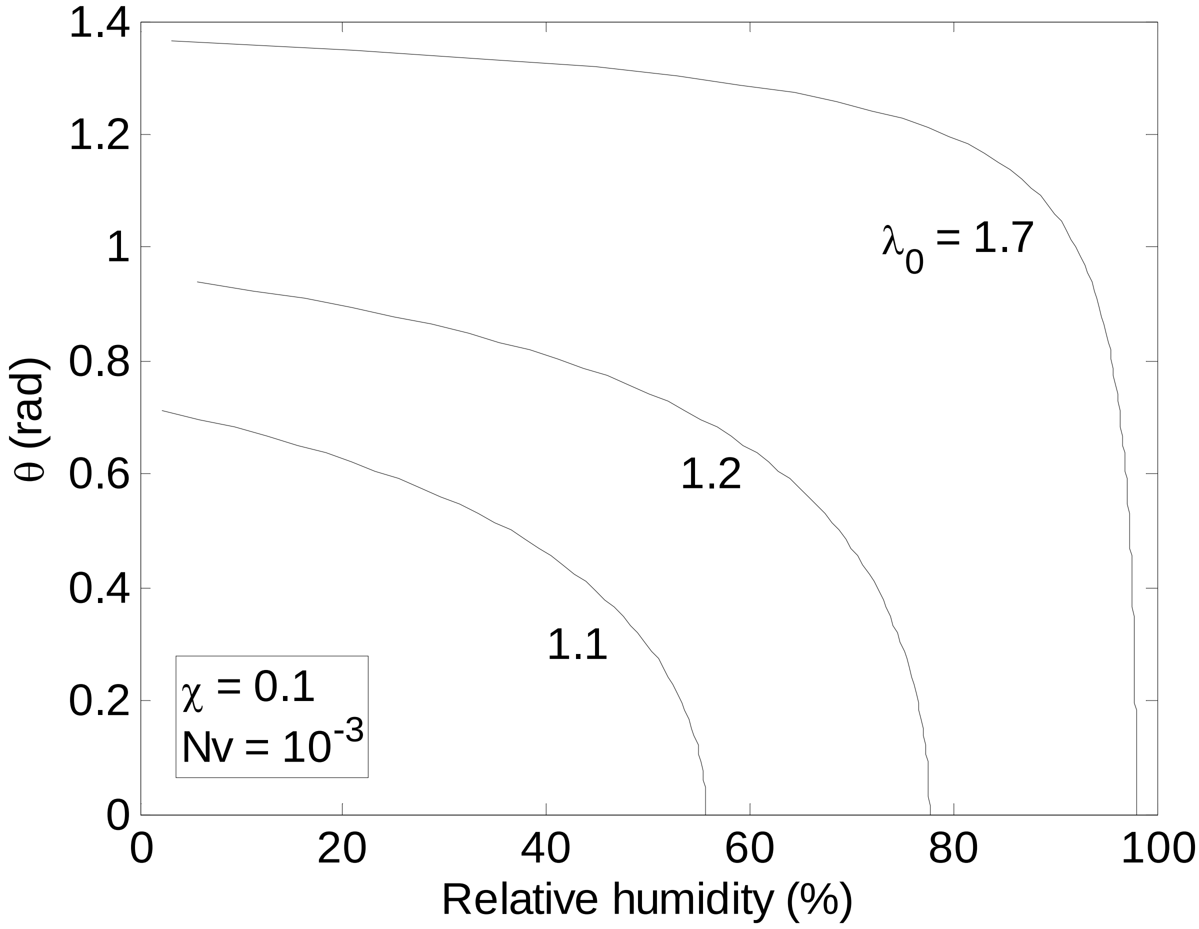




Experiment: Sidorenko, Krupenin, Taylor, Fratzl, Aizenberg, Science 315, 487 (2007).

Theory: Hong, Zhao, Suo, http://imechanica.org/node/2487

Critical humidity can be tuned

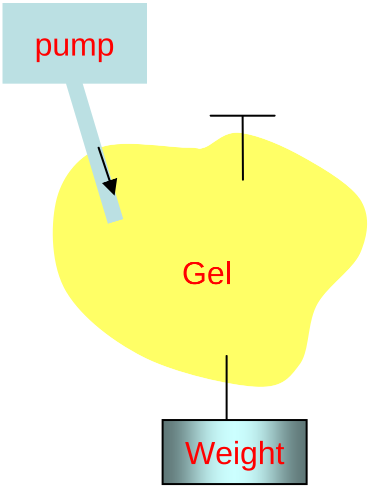


Hong, Zhao, Suo, http://imechanica.org/node/2487

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



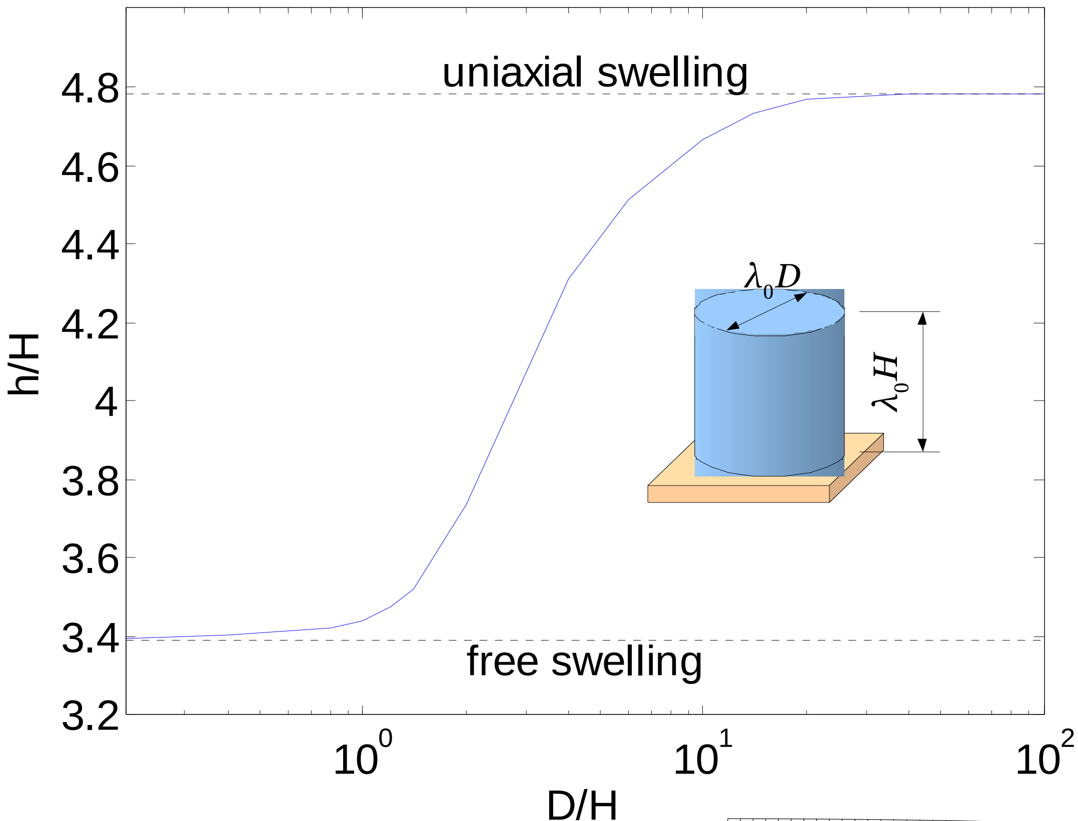
$$\int \delta \hat{W} dV = \int B_i \delta x_i dV + \int T_i \delta x_i dA$$

- A gel in equilibrium is analogous to elasticity
- Treat the chemical potential like temperature
- ABAQUS UMAT

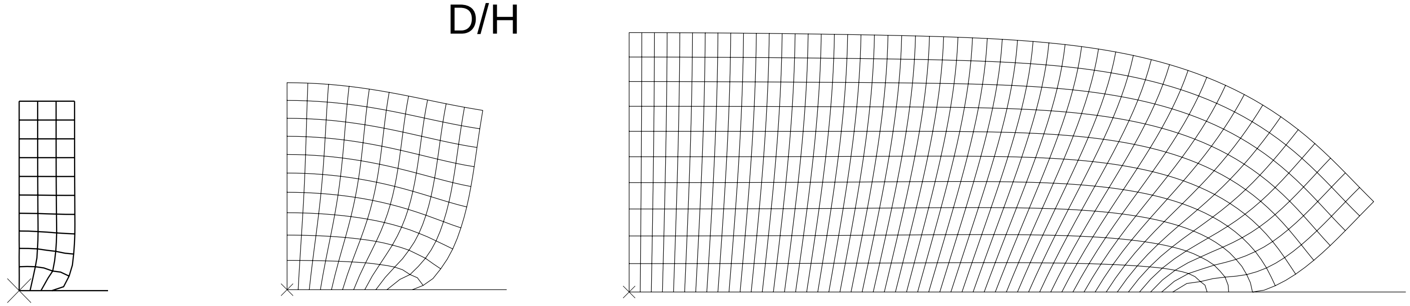
$$\hat{W}(\mathbf{F}, \mu) = W - \mu C = \frac{1}{2} NkT(I - 3 - 2\log J) - \frac{kT}{v}\left[(J-1)\log\frac{J}{J-1} + \frac{\chi}{J}\right] - \frac{\mu}{v}(J-1)$$

Hong, Liu, Suo, http://imechanica.org/node/3163

Swelling-induced contact

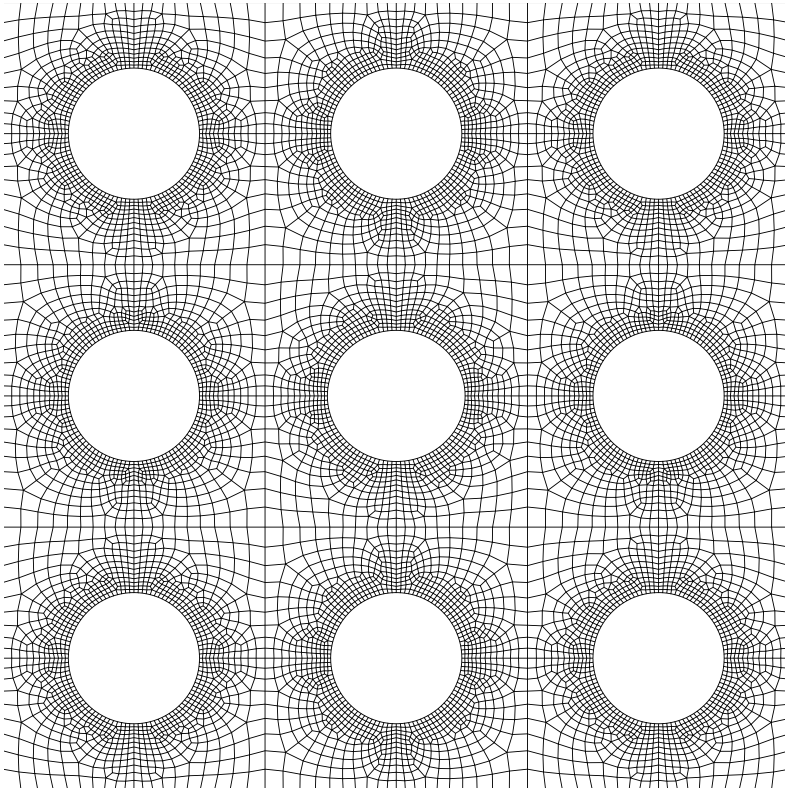


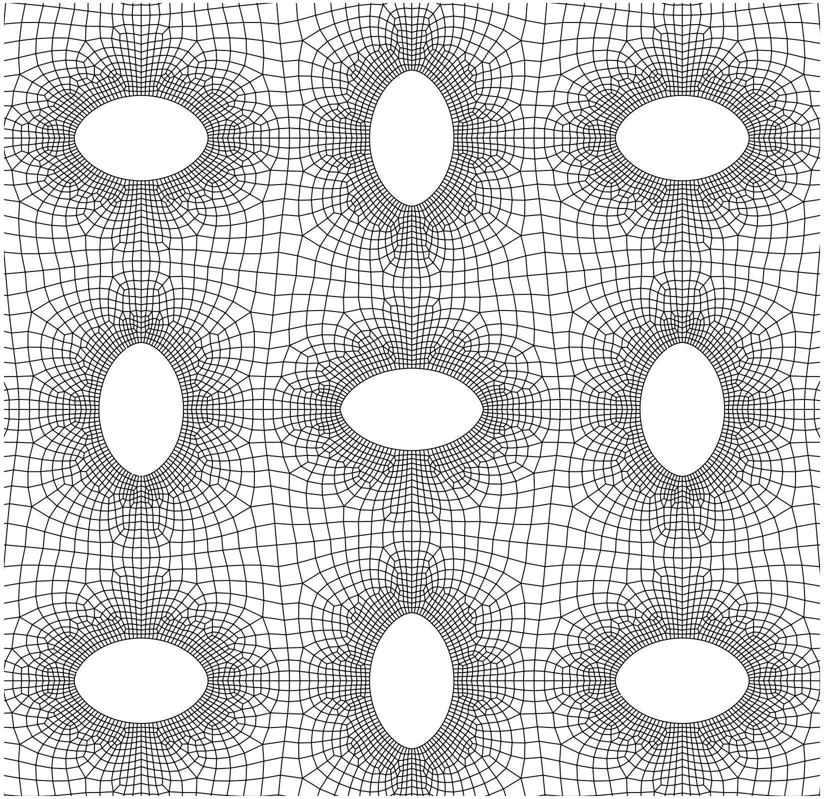
- Needle-like cylinder
- Pancake-like cylinder
- Contact



D/H = 0.6 D/H = 2 D/H = 10

Swelling-induced bifurcation

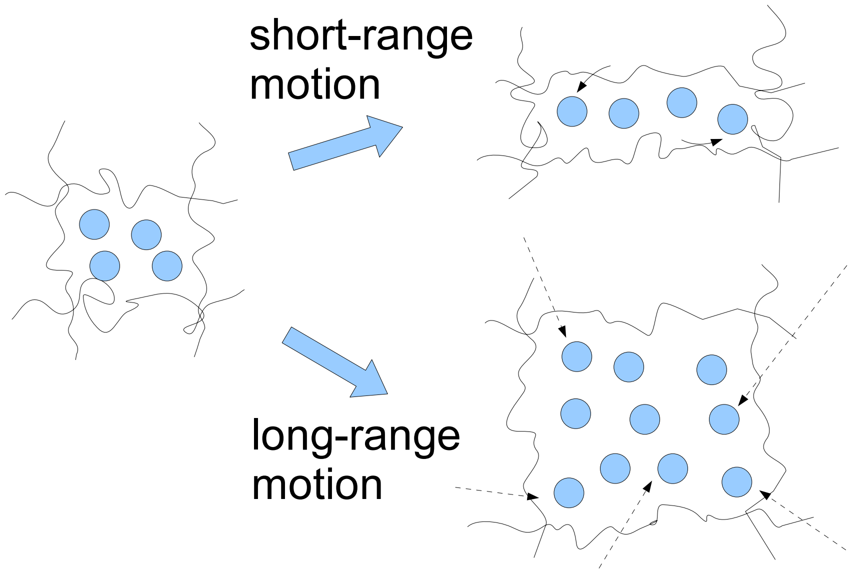




Experiment: Zhang, Matsumoto, Peter, Lin, Kamien, Yang, Nano Lett. 8, 1192 (2008).

Simulation: Hong, Liu, Suo, http://imechanica.org/node/3163

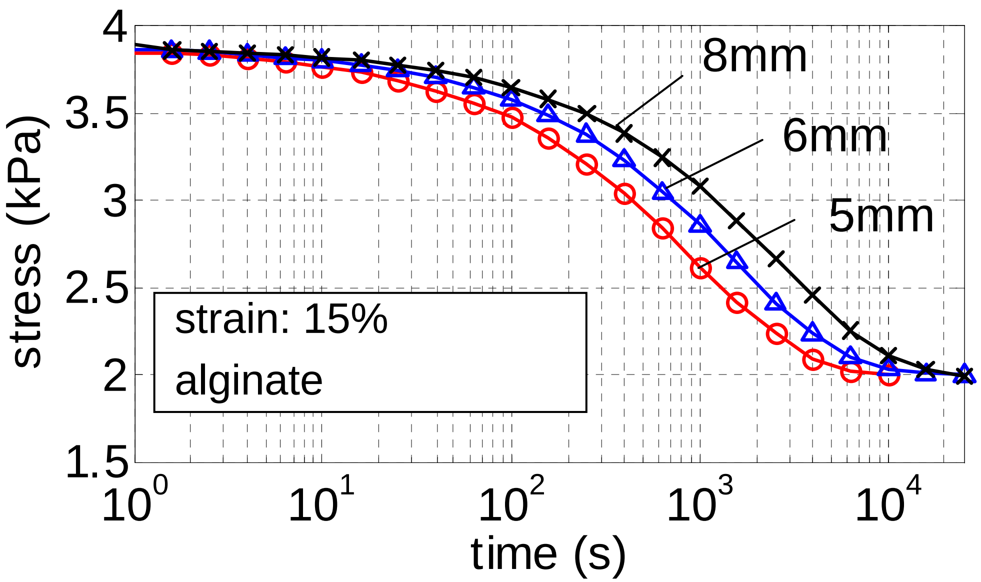
Time-dependent process

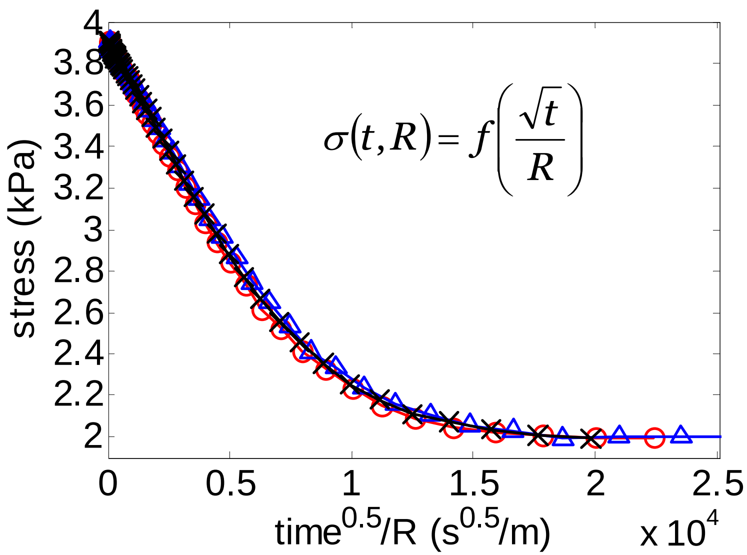


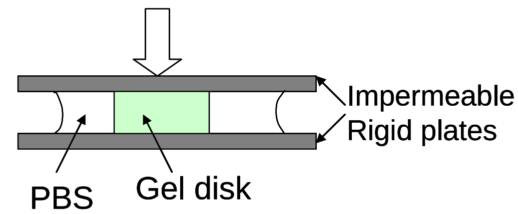
Shape change: short-range motion of solvent molecules, fast
Volume change: long-range motion of solvent molecules, slow

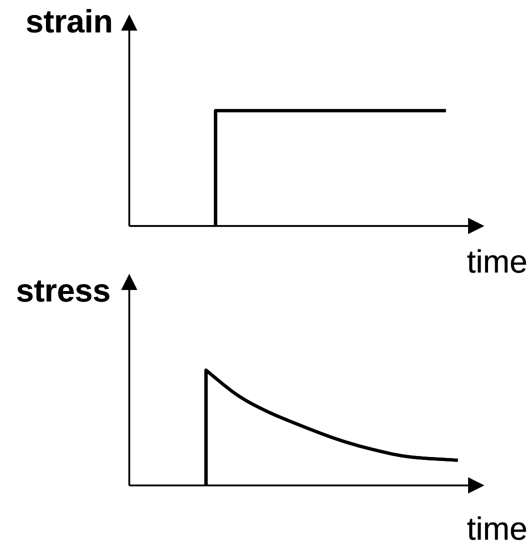
Hong, Zhao, Zhou, Suo, JMPS 56, 1779 (2008)

Size-dependent stress relaxation



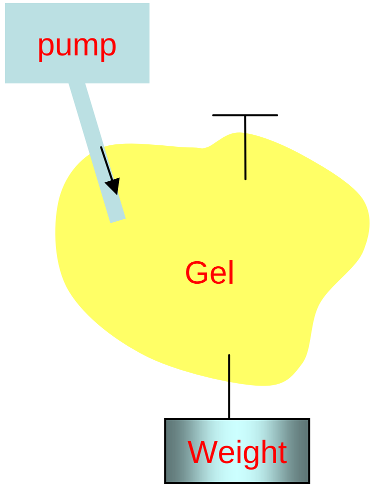






Zhao, Huebsch, Mooney, Suo, manuscript in preparation

Coupled deformation and migration



Deformation of network

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

Conservation of solvent molecules

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

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

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

$$s_{iK} = \frac{\partial W(\mathbf{F},C)}{\partial F_{iK}}$$

$$\mu = \frac{\partial W(\mathbf{F},C)}{\partial C}$$

Mechanical equilibrium

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

$$s_{iK} N_K = T_i$$

Rate process

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

Biot, JAP 12, 155 (1941)

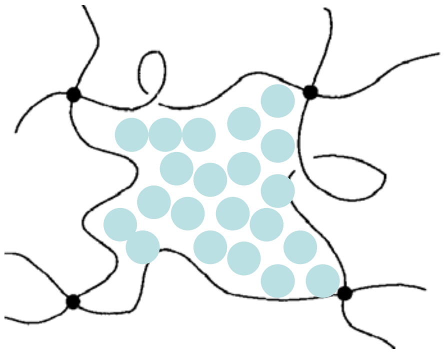
Hong, Zhao, Zhou, Suo, JMPS 56, 1779 (2008)

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

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

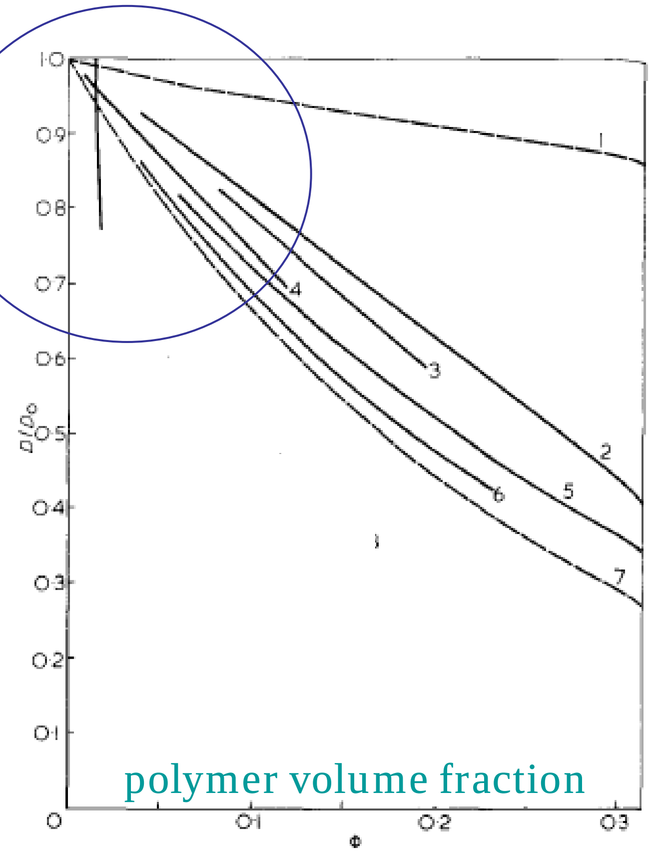
$$M_{KL} = \frac{D}{\upsilon kT} H_{iK} H_{iL} \left(\det F - 1 \right)$$

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

Diffusion of labeled water

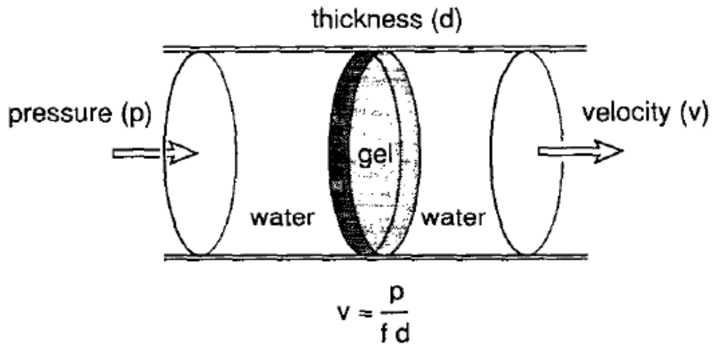
Stokes-Einstein formula

$$D_{\text{self}} = kT/(6\pi R\eta) \approx 8\times10^{-10}\,\text{m}^2/\text{s}$$

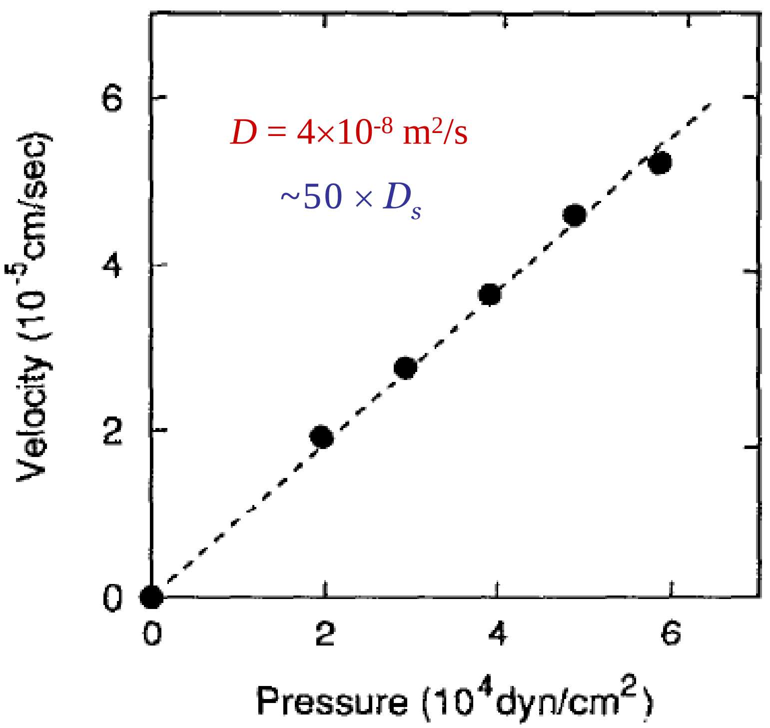


Muhr and Blanshard, Polymer, 1982

Diffusion or convection?



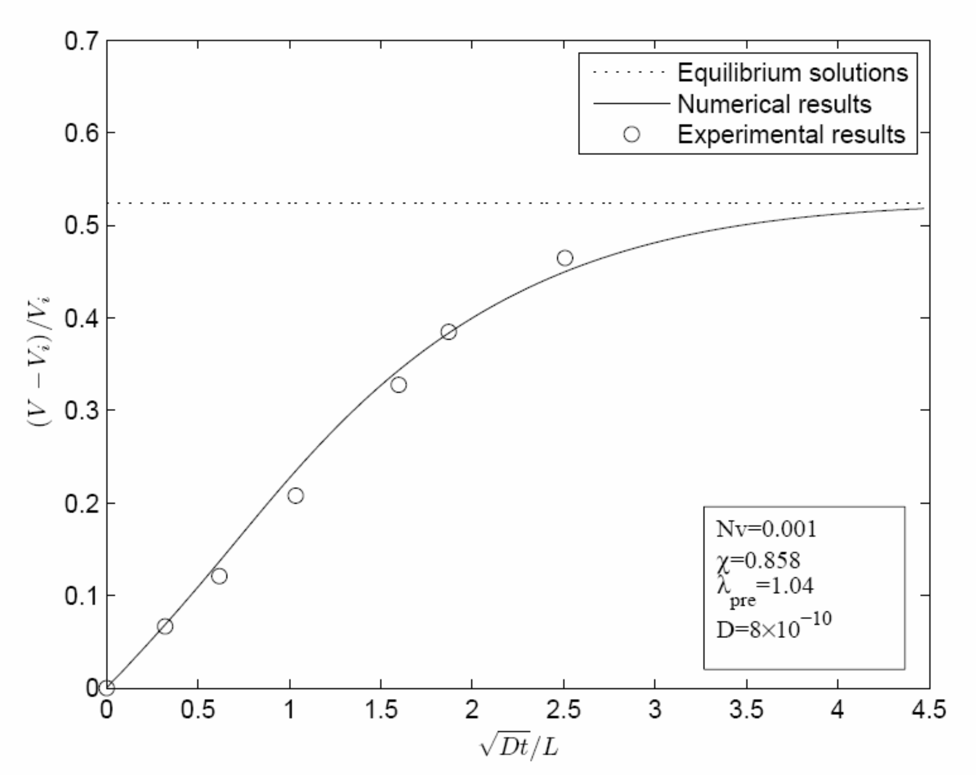
Tokita, Tanaka, J. Chem. Phys, 1991



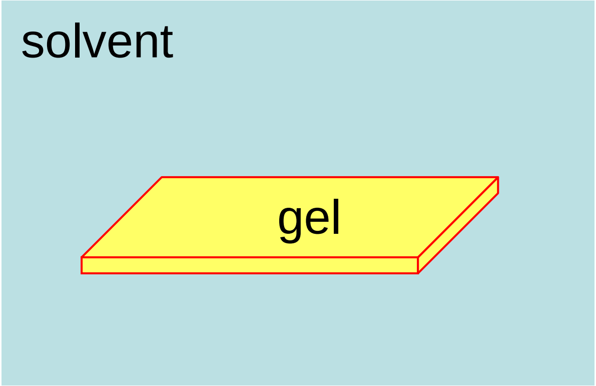
- Macroscopic pores?
- Convection?

Swelling of a thin layer

relative swelling



dimensionless time



Fitting swelling experiment is hard:

- Missing data
- Fick's law: Concentration is not the only driving force

Zhou, Zhao, Hong, Suo, unpublished work (2007)

Summary

- Gels have many uses (soft robots, drug delivery, tissue engineering, water treatment, packers in oil wells).
- Mechanics is interesting and challenging (large deformation, mass transport, multiple thermodynamic forces, many modes of instability).
- The field is wide open (microfabrication, computation, material models, experiments, bioinspiration, imagination).