Large deformation and instability in gels

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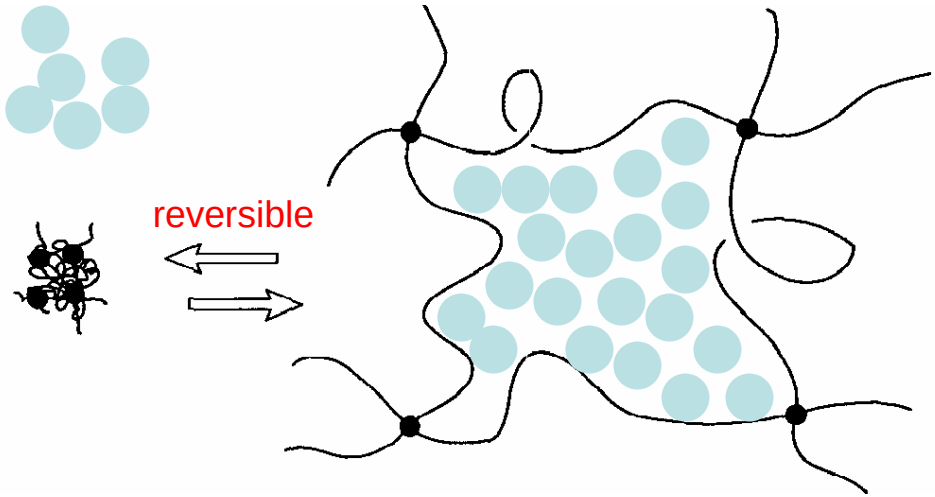
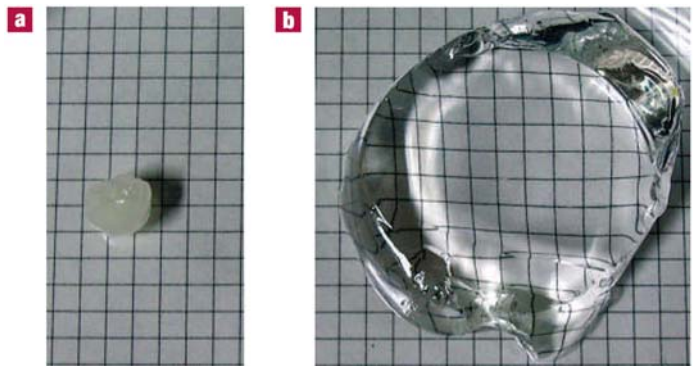
Gel = elastomer + solvent

Elasticity: long polymers are cross-linked by strong bonds.
Fluidity: polymers and solvent molecules aggregate by weak bonds.



Thermodynamics of swelling

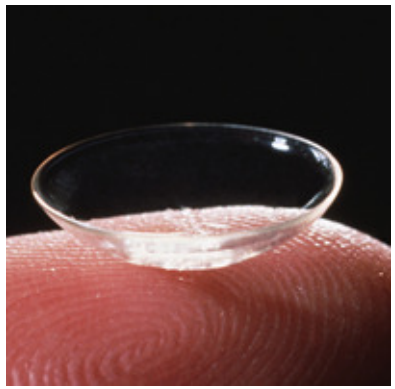
- Entropy of mixing
- Entropy of contraction
- Enthalpy of mixing



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

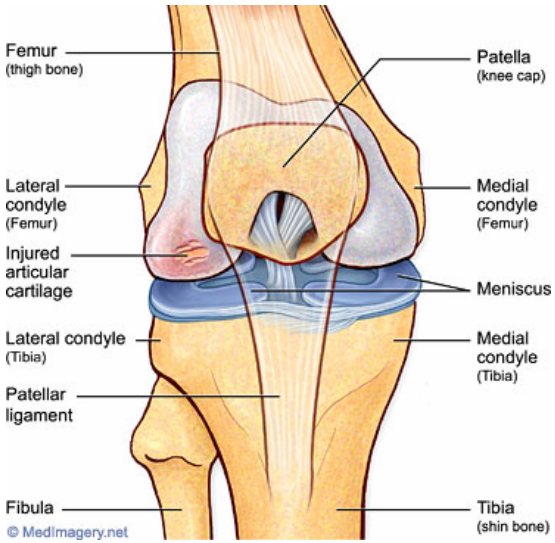
Gels in daily life

Jelly

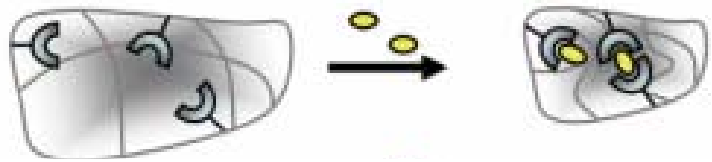


Contact lenses

Wichterie, Lim, Nature 185, 117 (1960)



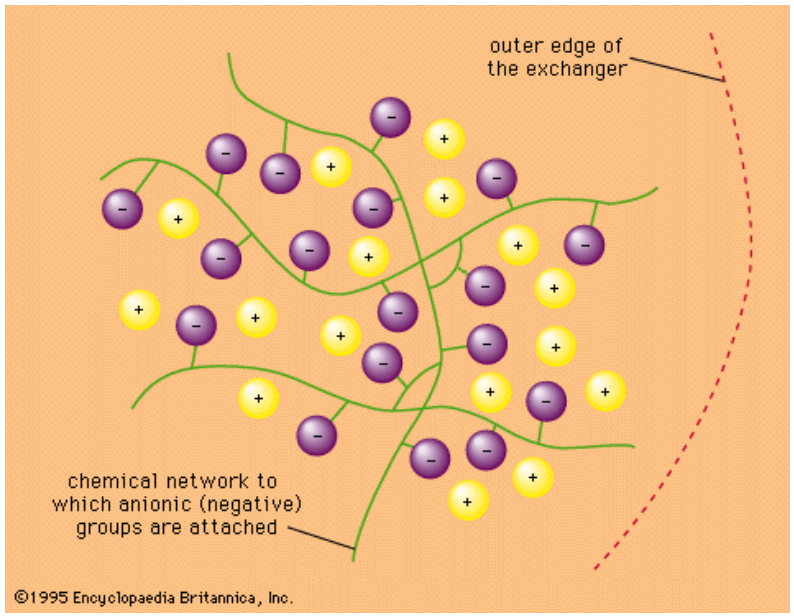
Tissues, natural or engineered



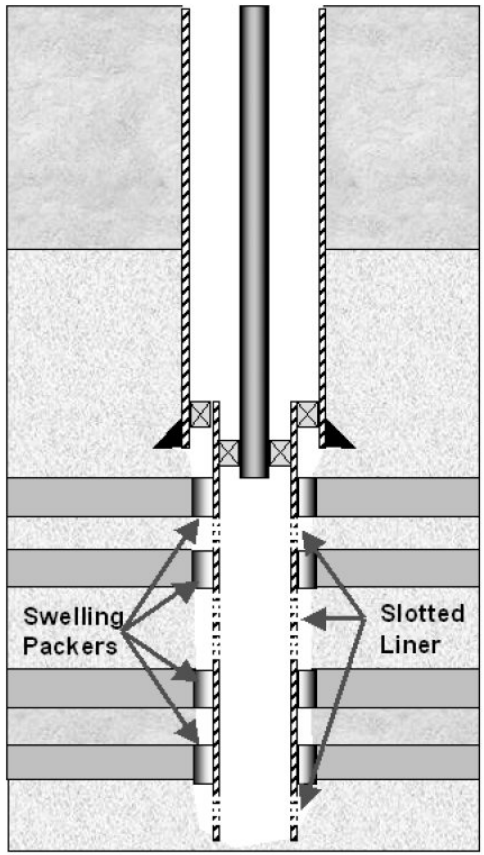
Drug delivery

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

Gels in engineering

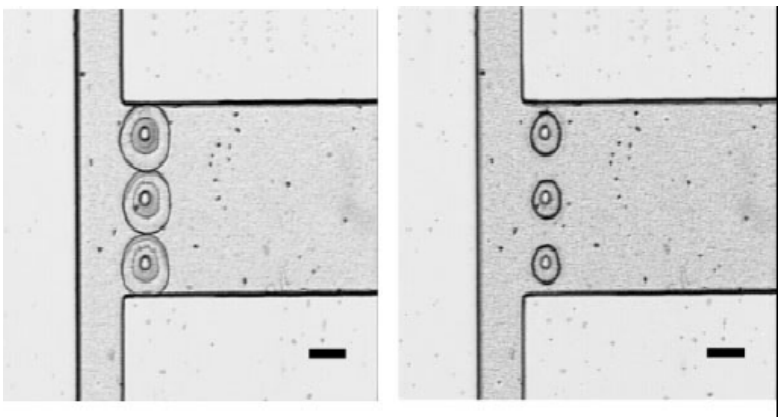


Ion exchange for water treatment



Sealing in oil wells

Shell, 2003



Valves in fluidics

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

THB theory

u_i - solid displacement

$\varepsilon_{ij} = \frac{1}{2}\left(u_{i,j} + u_{j,i}\right)$ - strain

$v_i = 0$ neglect liquid motion

Stress-strain relation

$$\sigma_{ij} = 2G\varepsilon_{ij} + \frac{2G\nu\varepsilon_{kk}}{1-2\nu}\delta_{ij}$$

Equilibrium equation

$$\sigma_{ij,j} - f\frac{\partial u_i}{\partial t} = 0$$

body force due to friction

Limitations

- No instant response to loads
- Linear theory, small deformation
- Basic principles are unclear, hard to extend

Tanaka, Hocker, and Benedek, J. Chem. Phys. 59, 5151 (1973)

Multiphasic theory

List of Equations biphasic theory

A nonionic polymeric gel is a mixture of two phases: network (n) and solvent (s).

Mass conservation

$$\frac{\partial \rho^n}{\partial t} + \nabla \cdot \left(\rho^n \mathbf{v}^n \right) = 0$$

$$\frac{\partial \rho^s}{\partial t} + \nabla \cdot \left(\rho^s \mathbf{v}^s \right) = 0$$

Balance of linear momentum

$$\rho^n \frac{D^n \mathbf{v}^n}{Dt} = \nabla \cdot \boldsymbol{\sigma}^n + \rho^n \mathbf{b}^n + \boldsymbol{\pi}^n$$

$$\rho^s \frac{D^s \mathbf{v}^s}{Dt} = \nabla \cdot \boldsymbol{\sigma}^s + \rho^s \mathbf{b}^s + \boldsymbol{\pi}^s$$

where the material derivative with respect to phase α

$$\frac{D^\alpha}{D} = \frac{\partial}{\partial t} + \mathbf{v}^\alpha \cdot \nabla ,$$

and $\boldsymbol{\pi}^\alpha$ is the momentum supply to α component from the other phase

$$\boldsymbol{\pi}^n + \boldsymbol{\pi}^s = \mathbf{o}$$

Energy conservation

$$\rho^n \frac{D^n e^n}{Dt} = \boldsymbol{\sigma}^n : \nabla \mathbf{v}^n - \nabla \cdot \mathbf{q}^n + \rho^n r^n + \varepsilon^n$$

$$\rho^s \frac{D^s e^s}{Dt} = \boldsymbol{\sigma}^s : \nabla \mathbf{v}^s - \nabla \cdot \mathbf{q}^s + \rho^s r^s + \varepsilon^s$$

Second law of thermodynamics

$$\rho^n \frac{D^n s^n}{Dt} + \nabla \cdot \frac{\mathbf{q}^n}{T} - \rho^n \frac{r^n}{T} + \rho^s \frac{D^s s^s}{Dt} + \nabla \cdot \frac{\mathbf{q}^s}{T} - \rho^s \frac{r^s}{T} \geq 0$$

where s^α is the entropy density of α component, and the Helmholtz free energy density

$$A^n = e^n - T s^n = A^n \left(T, \mathbf{C}, \rho^n, \rho^s \right)$$

$$A^s = e^s - T s^s = A^s \left(T, \mathbf{C}, \rho^n, \rho^s \right)$$

Incompressibility

$$\varphi^n \nabla \cdot \mathbf{v}^n + \varphi^s \nabla \cdot \mathbf{v}^s + \left(\mathbf{v}^s - \mathbf{v}^n \right) \cdot \nabla \varphi^s = 0$$

where the volume fraction φ^α is related to the density as $\rho^\alpha = \varphi^\alpha \rho_0^\alpha$.

The constitutive relations:

$$\boldsymbol{\sigma}^n = -\varphi^n \lambda \mathbf{I} + 2\mathbf{F} \cdot \left(\rho^n \frac{\partial A^n}{\partial \mathbf{C}} + \rho^s \frac{\partial A^s}{\partial \mathbf{C}} \right) \cdot \mathbf{F}^T$$

$$\boldsymbol{\sigma}^s = -\varphi^s \lambda \mathbf{I} - \rho^s \left(\rho^n \frac{\partial A^n}{\partial \rho^s} + \rho^s \frac{\partial A^s}{\partial \rho^s} \right) \mathbf{I}$$

$$\boldsymbol{\pi}^n = -\boldsymbol{\pi}^s = \lambda \nabla \varphi^n - \rho^n \frac{\partial A^n}{\partial \rho^s} \nabla \rho^s + \rho^s \nabla \mathbf{C} : \frac{\partial A^s}{\partial \mathbf{C}} + \mathbf{f} \left(\mathbf{v}^s - \mathbf{v}^n \right)$$

Helmholtz free energy for each species

$$A^n = e^n - T s^n = A^n \left(T, \mathbf{C}, \rho^n, \rho^s \right)$$

$$A^s = e^s - T s^s = A^s \left(T, \mathbf{C}, \rho^n, \rho^s \right)$$

Is the theory applicable to gels?

- View solvent and solute as two phases
- Unclear physical picture.
- Unmeasurable quantities.

Bowen, Int. J. Eng. Sci. (1980)
Lai, Hou, Mow, J. Biomech. Eng. Trans. (1991)

Our preference: monophasic theory

- Regard a gel as a single phase.
- Start with thermodynamics.

Gibbs, The Scientific Papers of J. Willard Gibbs, pp. 184, 201, 215 (1878):
Derive equilibrium theory from thermodynamics. (This part of his work seems less known.)
Biot, JAP 12, 155 (1941): Use Darcy's law to model migration. Poroelasticity.
……

Hong, Zhao, Zhou, Suo, JMPS (2007). http://dx.doi.org/10.1016/j.jmps.2007.11.010

System = gel + weight + solvent

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

$P\delta l$ work done by the weight

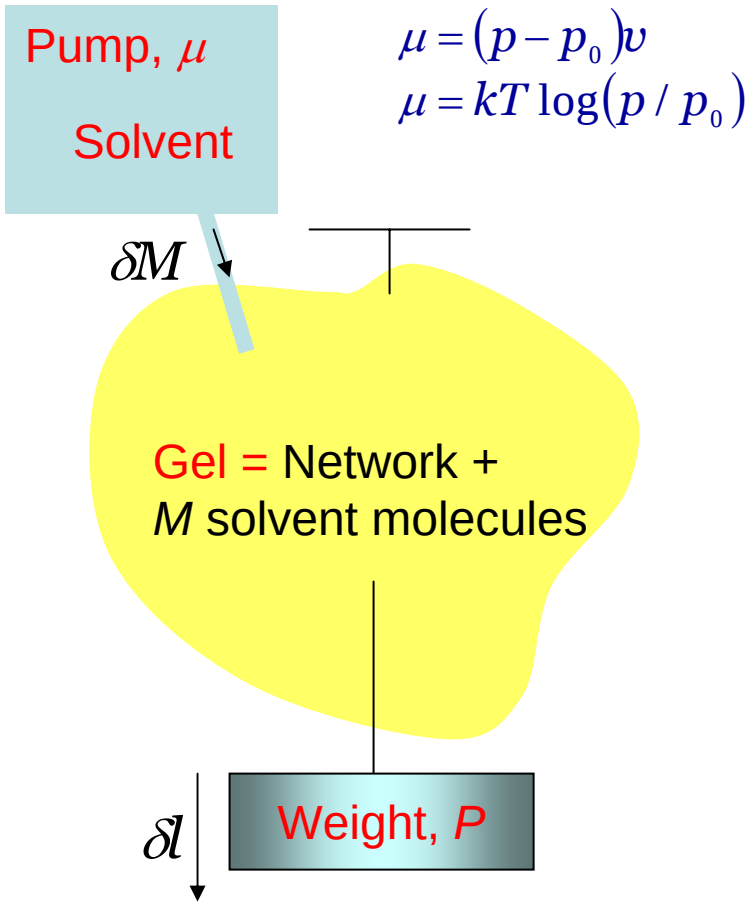
$F(l, M)$ Helmholtz free energy of gel

Equilibrium condition

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

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

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



Field variables

Equilibrium condition

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

$$\lambda = \frac{l}{L} \qquad C = \frac{M}{AL} \qquad s = \frac{P}{A}$$

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

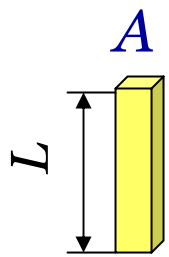
$$\delta W = s\delta\lambda + \mu\delta C$$

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

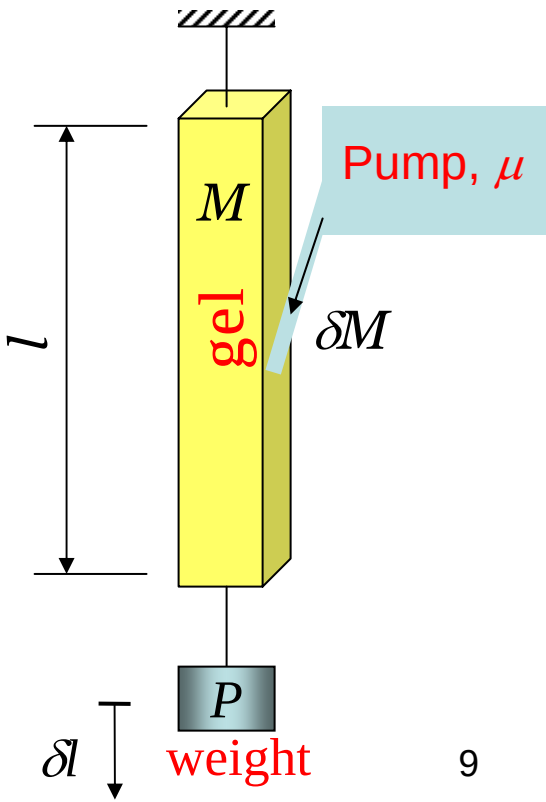
$W(\lambda, C)$ Helmholtz free energy per volume

Reference state

$M = 0$



Current state



3D inhomogeneous field

Deformation gradient

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

Concentration

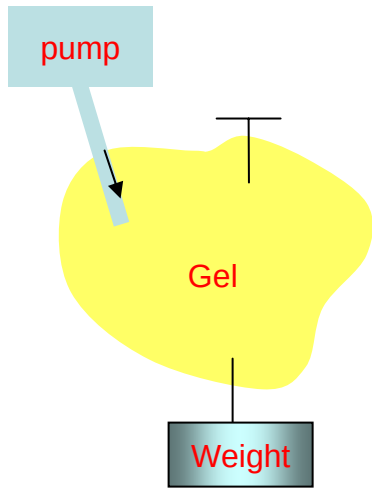
$$C(\mathbf{X},t)$$

Free-energy function

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

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

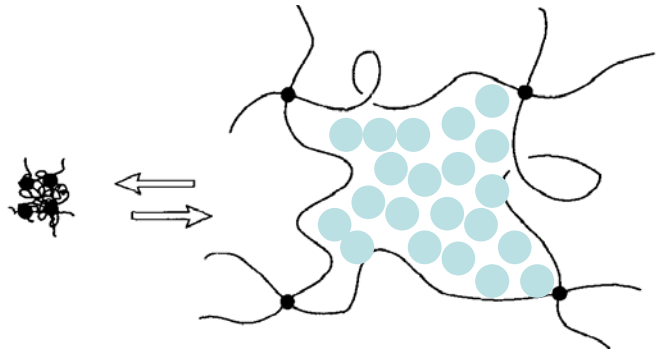
$$s_{iK} = \frac{\partial W(\mathbf{F},C)}{\partial F_{iK}} \qquad \mu = \frac{\partial W(\mathbf{F},C)}{\partial C}$$

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

Gibbs (1878)

Flory-Rehner free energy

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



Free-energy function

$$W(\mathbf{F},C)=W_s(\mathbf{F})+W_m(C)$$

Free energy of stretching

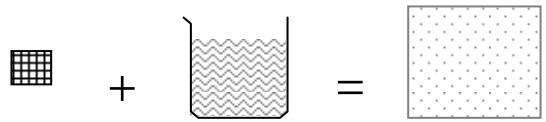
$$W_s(\mathbf{F})=\tfrac{1}{2}NkT\left[F_{iK}F_{iK}-3-2\log(\det\mathbf{F})\right]$$

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.
- 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

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

Use the Flory-Rehner free energy

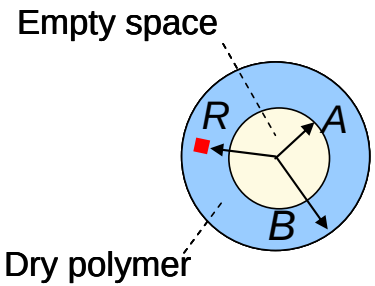
$$s_{iK} = NkT(F_{iK} - H_{iK}) - \Pi H_{iK} \det \mathbf{F} \qquad \mu = kT\left[\log\frac{vC}{1+vC} + \frac{1}{1+vC} + \frac{\chi}{(1+vC)^2}\right] + \Pi v$$

$$s_1 = NkT\left(\lambda_1 - \lambda_1^{-1}\right) - \Pi\lambda_2\lambda_3$$

$$s_2 = NkT\left(\lambda_2 - \lambda_2^{-1}\right) - \Pi\lambda_3\lambda_1$$

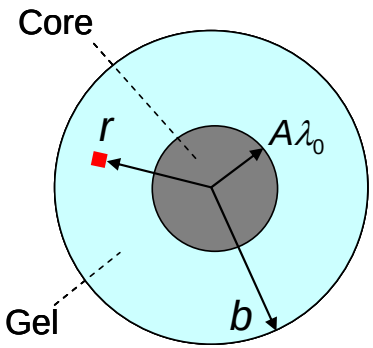
$$s_3 = NkT\left(\lambda_3 - \lambda_3^{-1}\right) - \Pi\lambda_1\lambda_2$$

Inhomogeneous equilibrium state



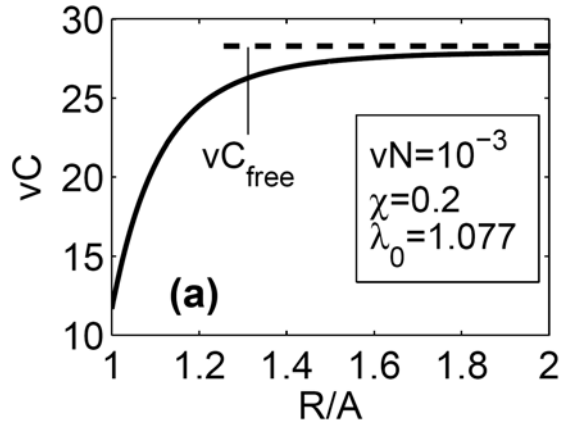
(a)

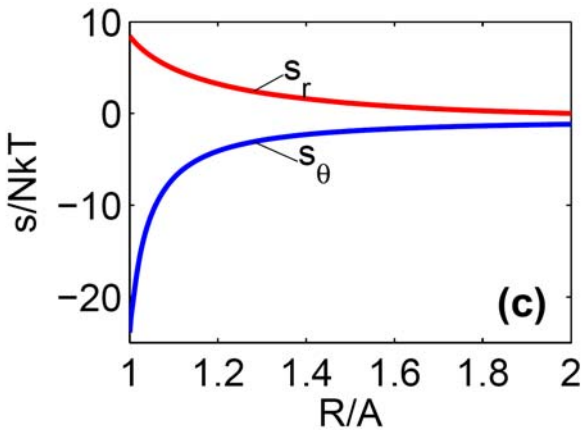
Reference State



(b)

Equilibrium State

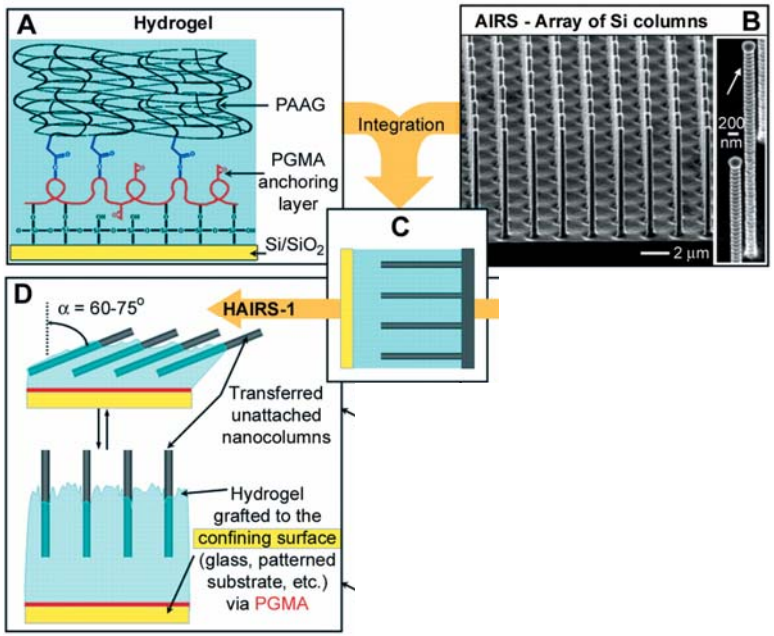


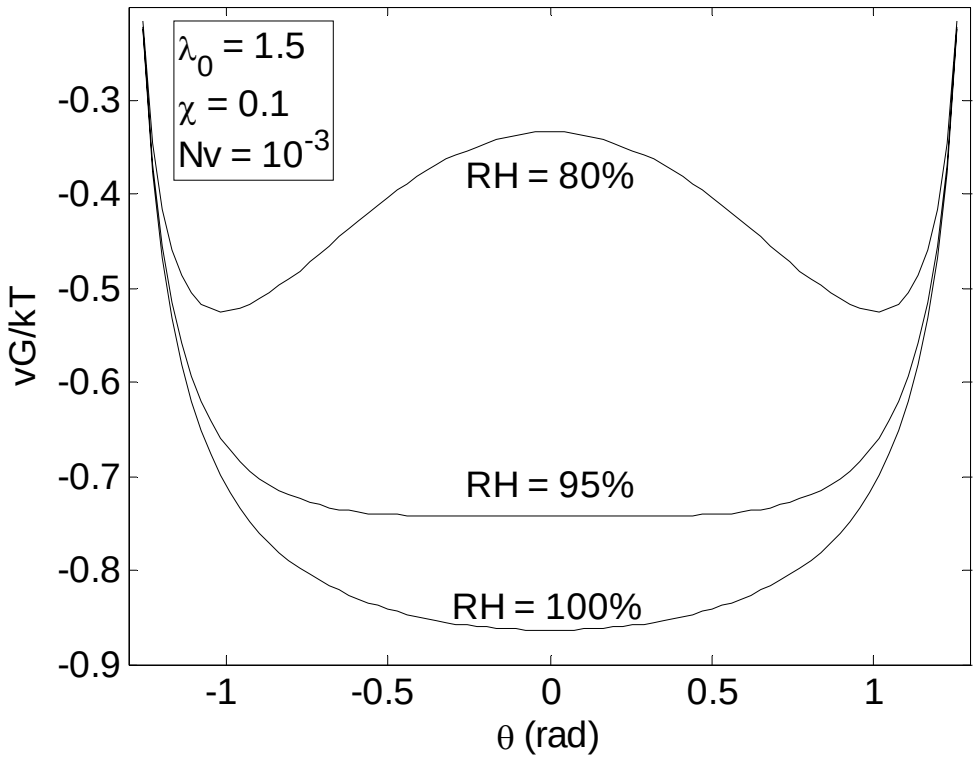


- Concentration is inhomogeneous even in equilibrium.
- Stress is high near the interface (debonding, cavitation, wrinkles).

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

Hydrogel-actuated nanostructure

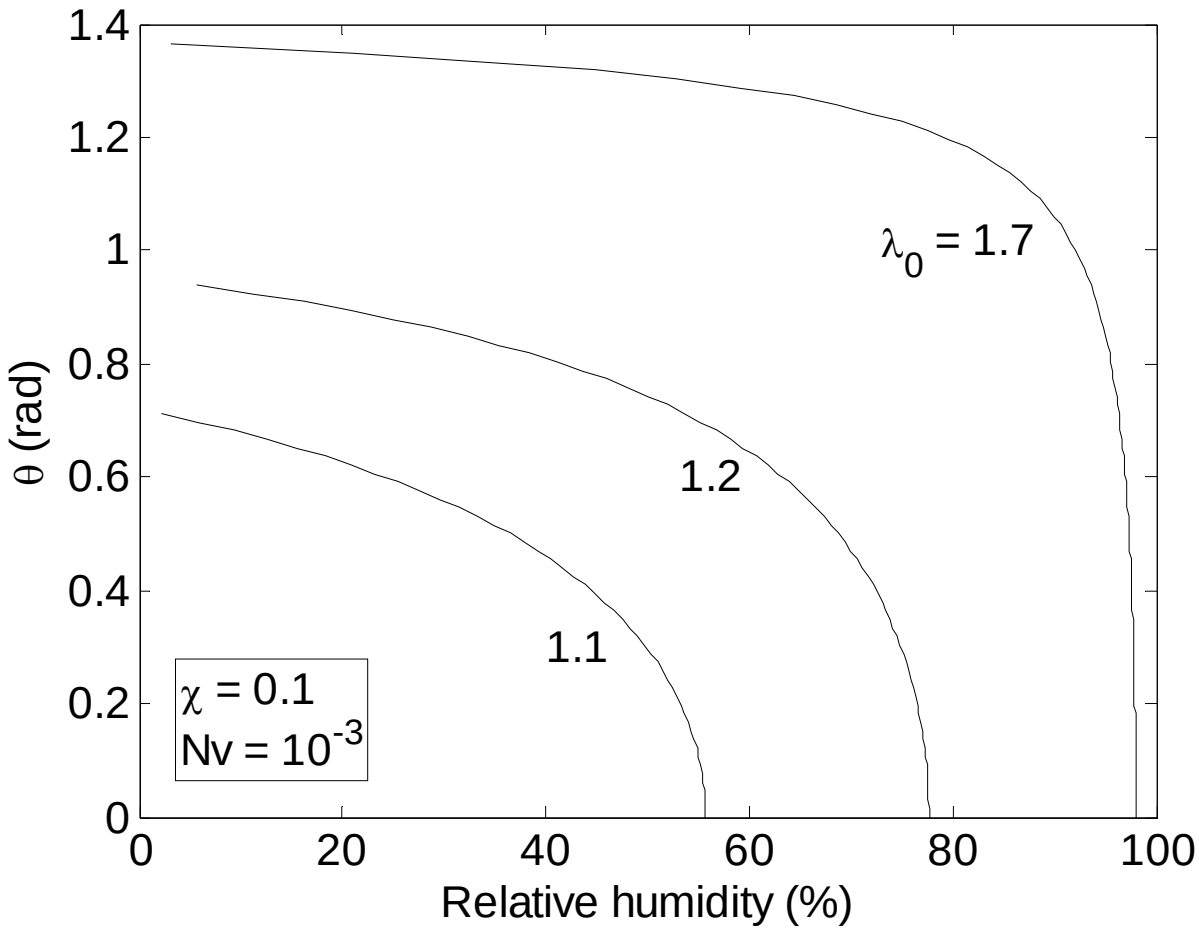




Experiment: Sidorenko, Krupenin, Taylor, Fratzl, Aizenberg, Science 315, 487 (2007).

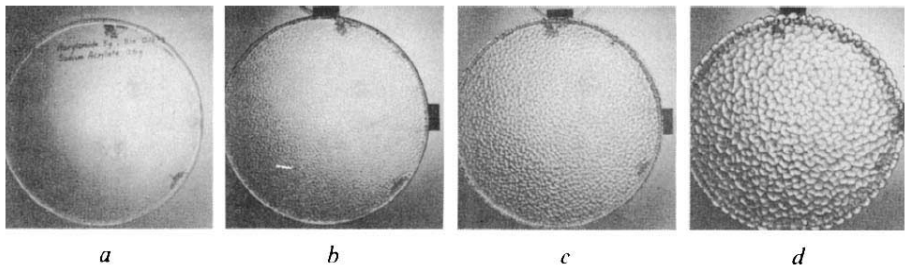
Theory: Hong, Zhao, Suo, http://imechanica.org/node/2487

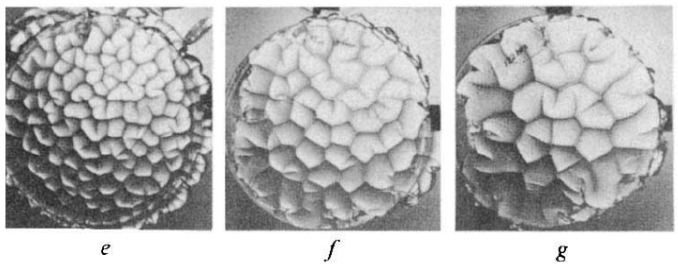
Critical humidity can be tuned



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

Crease

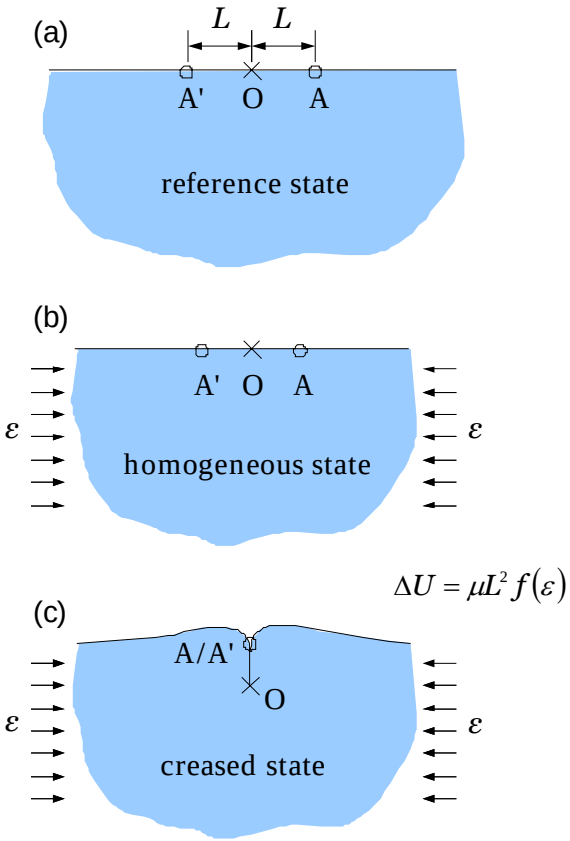


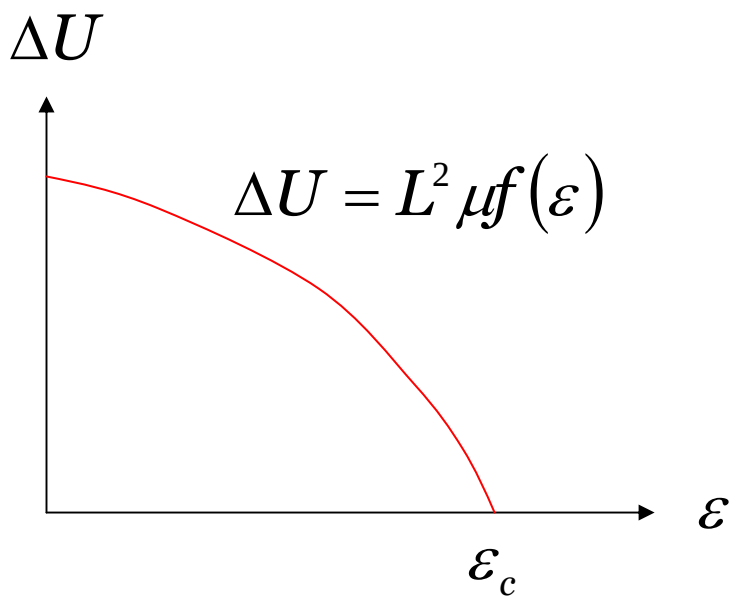


Tanaka *et al*, Nature 325, 796 (1987)

Denian

Our model





Linear perturbation, Biot (1963), $\varepsilon_{biot} \approx 0.46$

Experiment, Gent, Cho, *Rubber Chemistry and Technology* 72, 253 (1999)

Our model $\varepsilon_c \approx 0.35$

Elasticity with huge volumetric change

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

An alternative free-energy function $$\hat{W} = W - \mu C$$

Recall $$\delta W = s_{iK} \delta F_{iK} + \mu \delta C$$

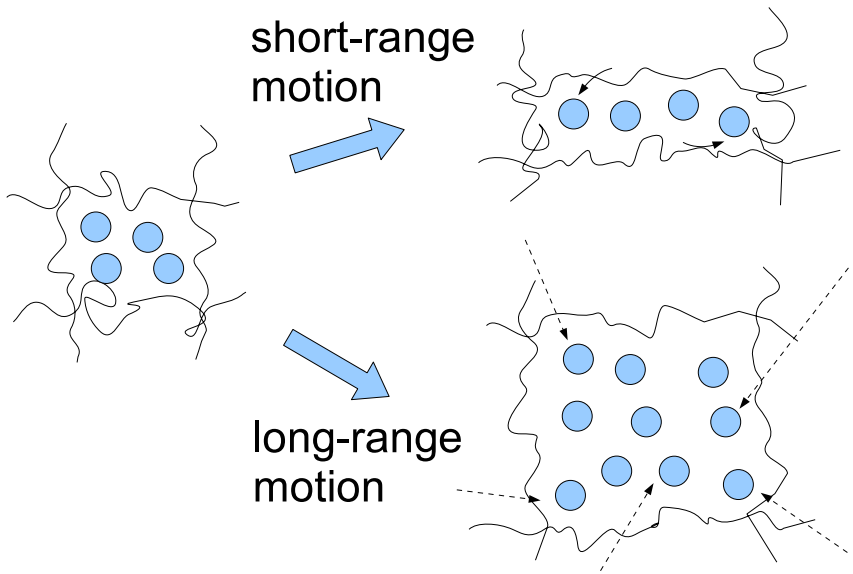
$$\delta \hat{W} = s_{iK} \delta F_{iK} - C \delta \mu$$

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

ABAQUS UMAT

Liu, Hong, Suo, manuscript in preparation.

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 (2007). http://dx.doi.org/10.1016/j.jmps.2007.11.010

Coupled deformation and migration

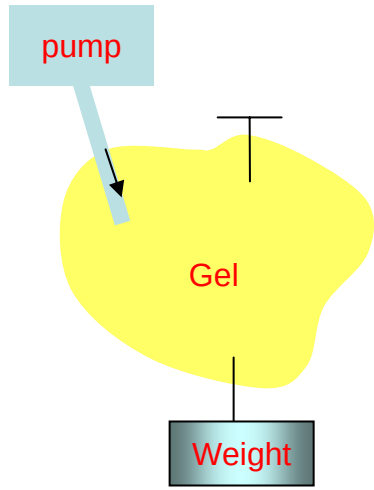
Deformation of network

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

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)

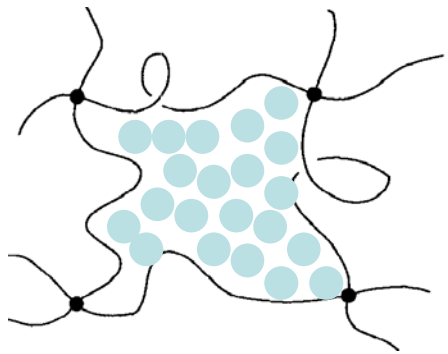
Hong, Zhao, Zhou, Suo, JMPS (2007). http://dx.doi.org/10.1016/j.jmps.2007.11.010

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 quant

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

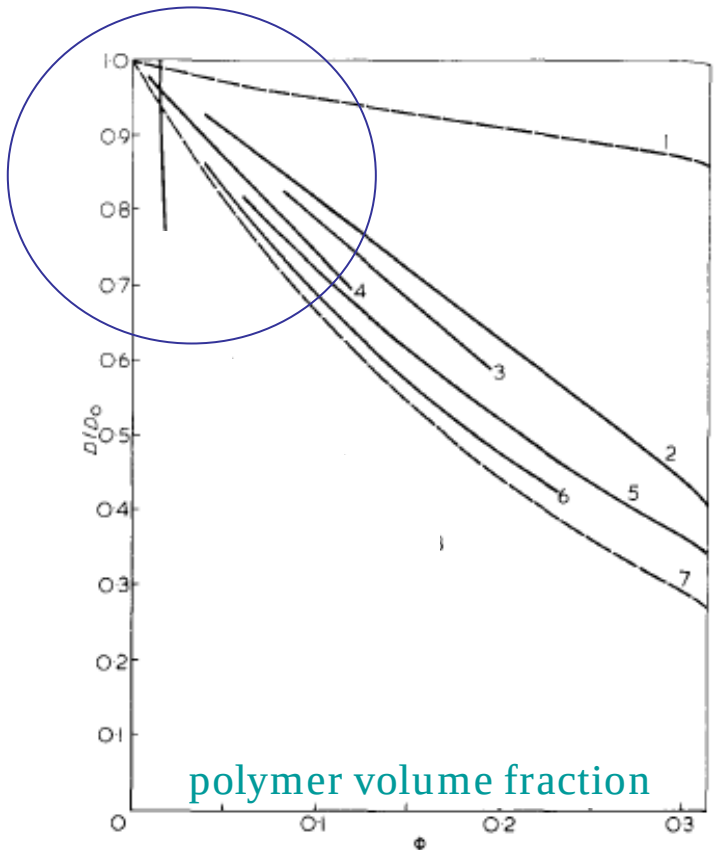
$$M_{KL} = \frac{D}{\upsilon kT} H_{iK} H_{iL} \left(\det F - 1\right)$$

Hong, Zhao, Zhou, Suo, JMPS (2007). http://dx.doi.org/10.1016/j.jmps.2007.11.010

Diffusion of labeled water

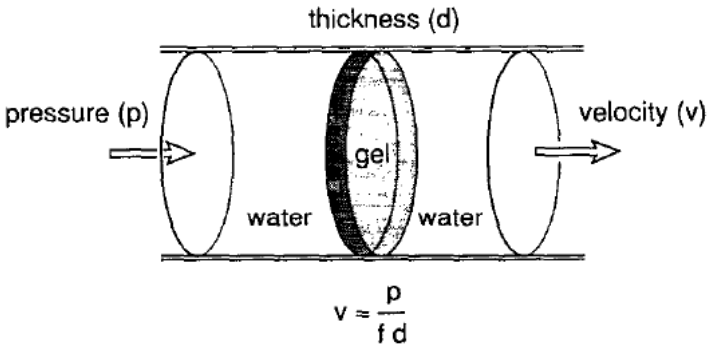
Stokes-Einstein formula

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

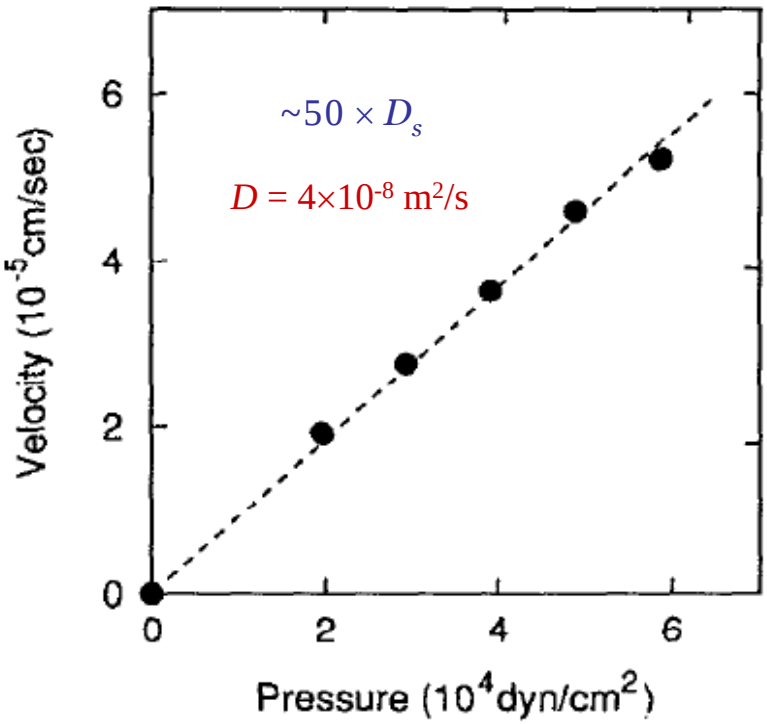


Muhr and Blanshard, Polymer, 1982

Diffusion or convection?

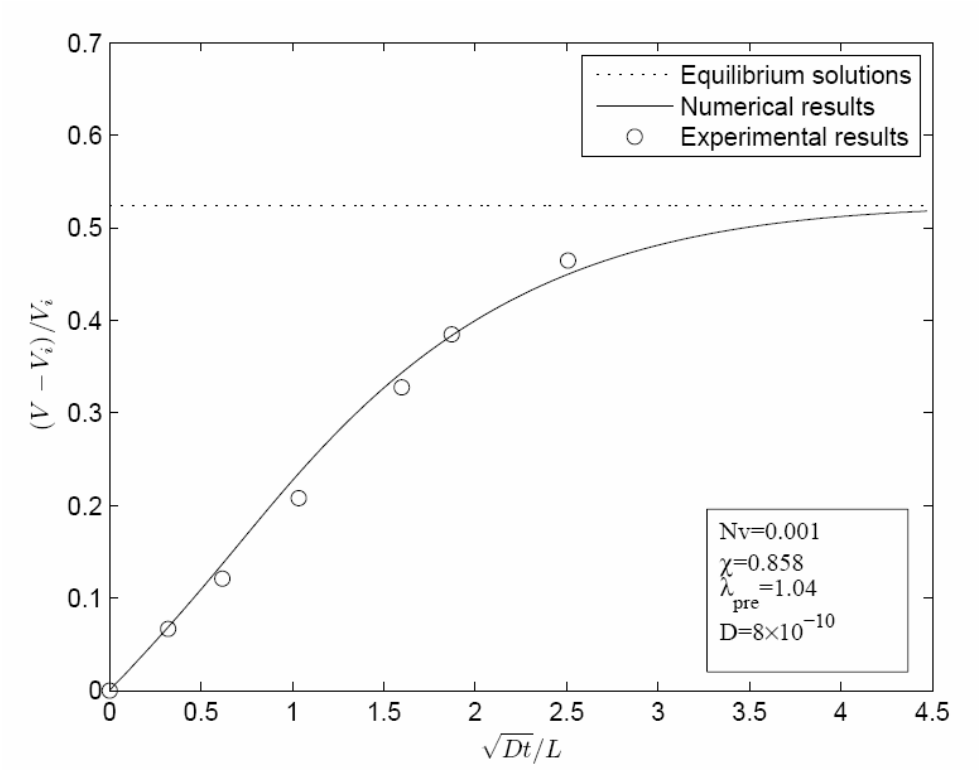


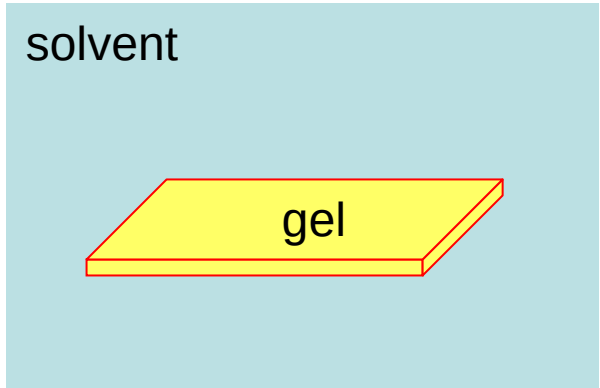
Tokita, Tanaka, J. Chem. Phys, 1991



- Macroscopic pores?
- Convection?

Swelling of a thin layer





Fitting swelling experiment is hard:

- Missing data
- Fick's law: Concentration is not the only driving force
- TBH theory also has problems

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

Summary

- Gels have many uses (soft robots, drug delivery, tissue engineering, water treatment, sealing in oil wells).
- Mechanics is interesting and challenging (large deformation, mass transport, thermodynamic forces, instabilities).
- The field is wide open.