

A membrane theory for swelling polymer gels

Alessandro Lucantonio

Joint work with Luciano Teresi and Antonio DeSimone



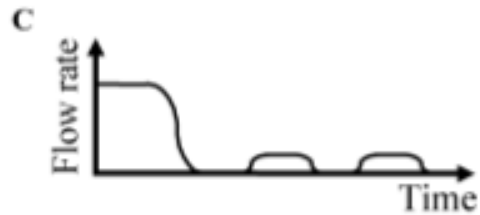
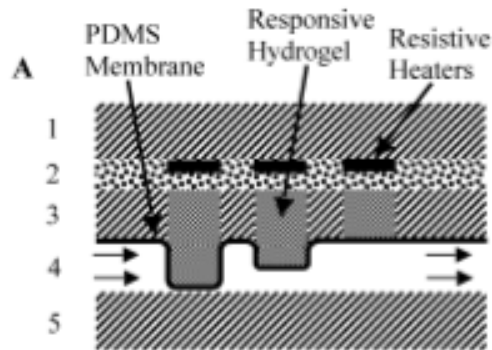
AdG "MicroMotility"



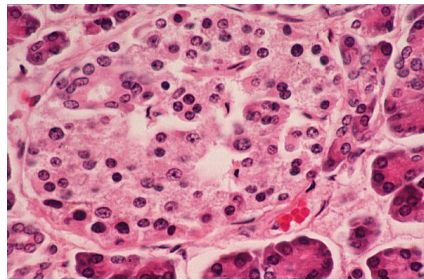
Physics and applications of polymer gels

A polymer gel is a soft elastic material consisting of a polymer network swollen with a fluid (solvent).

In *thermo-responsive* gels, the solvent-polymer chemical affinity varies with temperature and affects the swelling degree.



Actuators for microfluidics



Plants and biological tissues



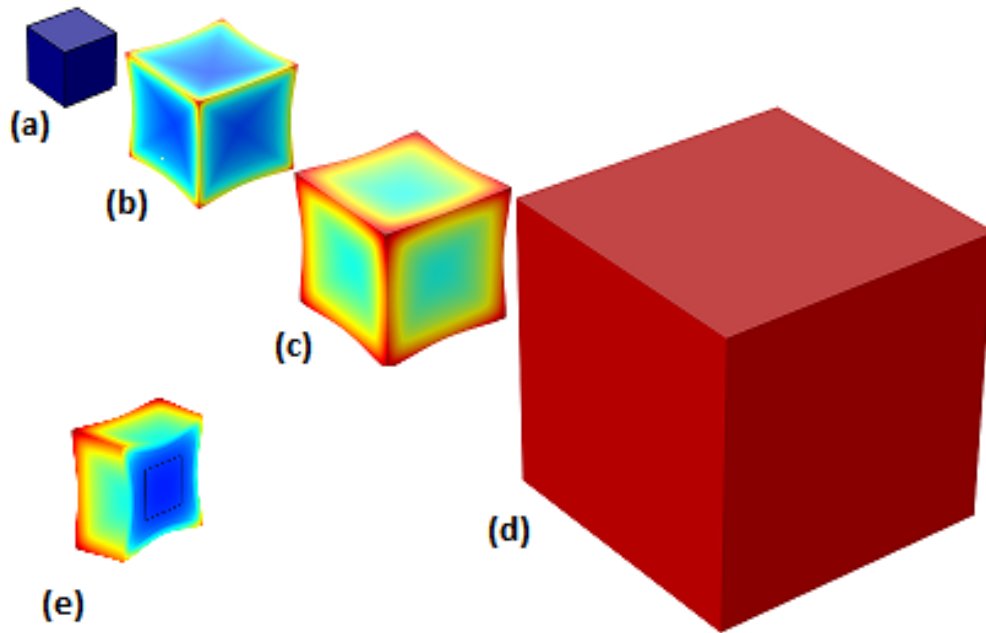
Contact lenses



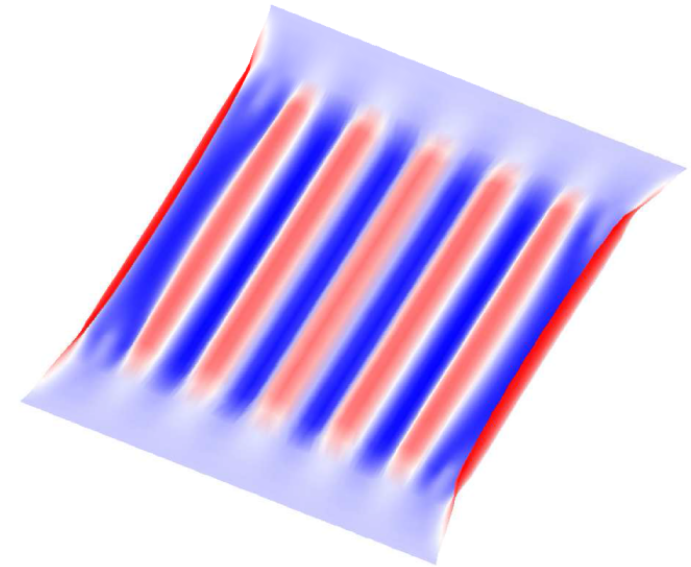
Drug delivery systems

Modeling of swelling-induced deformations

- ▶ **Non-linear 3D** models of coupled elasticity and solvent transport.
- ▶ **Structural** (reduced) models of polymer gels: *beams, plates, shells*.
- ▶ **Shape morphing and instabilities.**



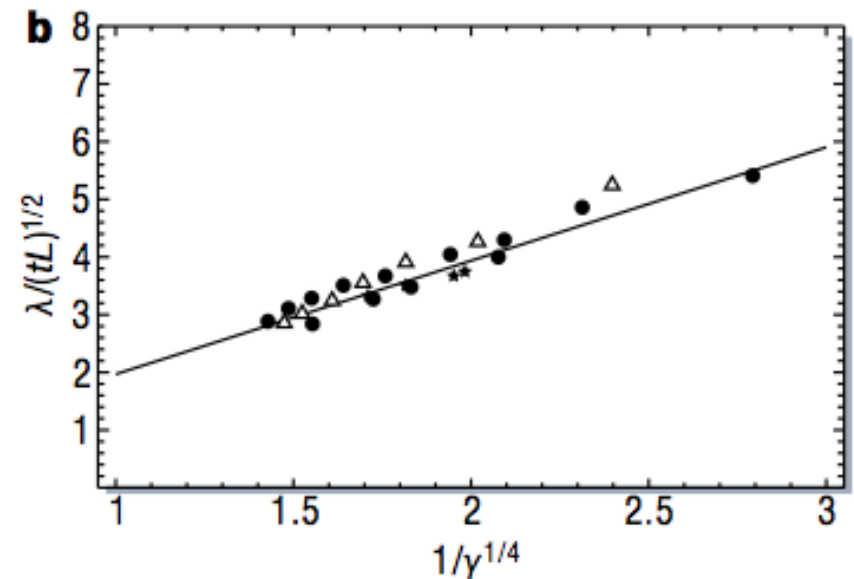
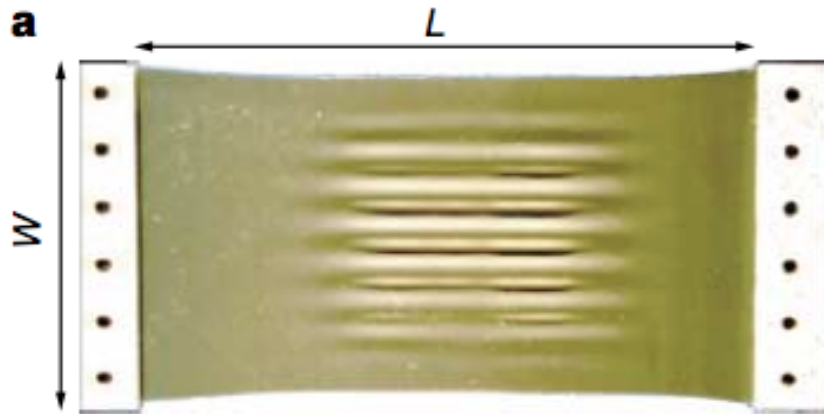
Transient free swelling of a cubic gel



Swelling-induced wrinkling of a stretched elastomeric membrane

A.L. et al., *Transient analysis of swelling-induced large deformations in polymer gels*, JMPS 61, 2013.
A.L. et al., *Buckling dynamics of a solvent-stimulated stretched elastomeric sheet*, Soft Matter 10, 2014.

Background: wrinkling of free-standing films

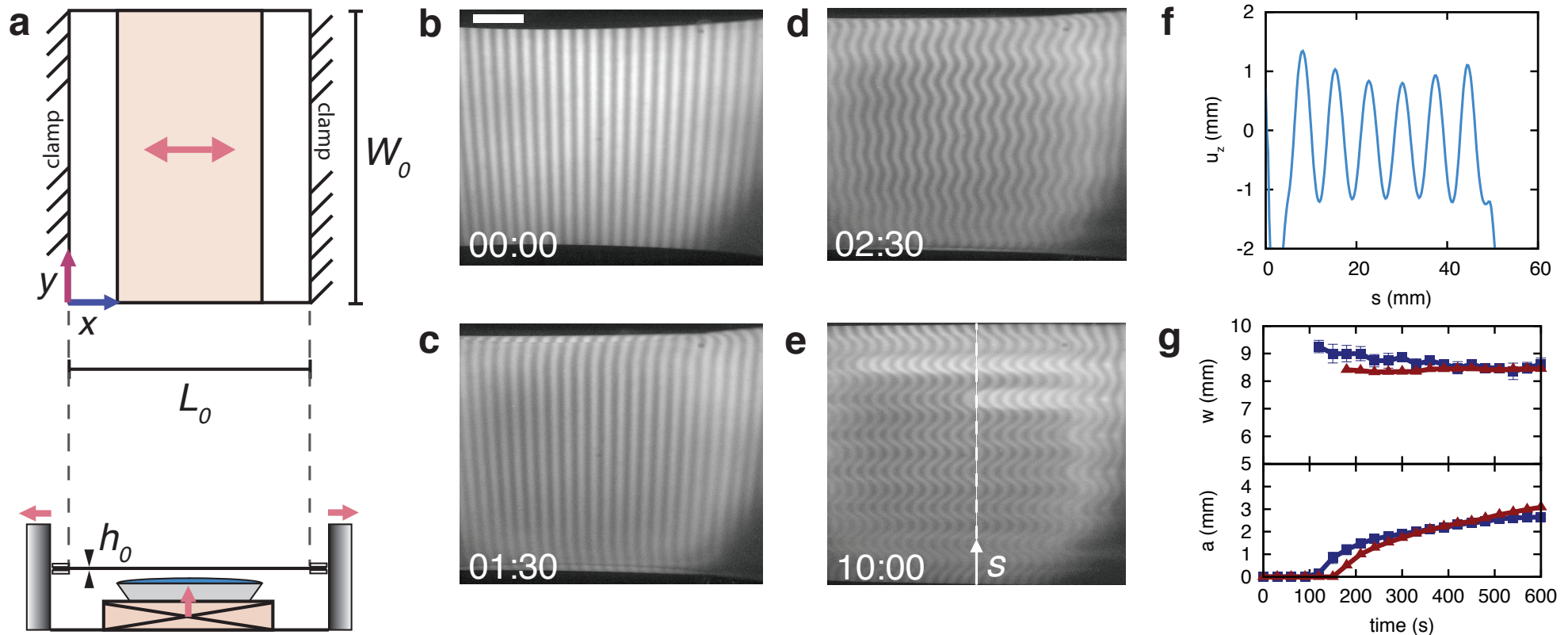


(from Cerda & Mahadevan, 2002)

- ▶ The wavelength follows a scaling law with applied strain
- ▶ For certain aspect ratios, wrinkling does not occur \rightarrow swelling-induced wrinkling
- ▶ **How can we combine swelling and stretching for shape control?**

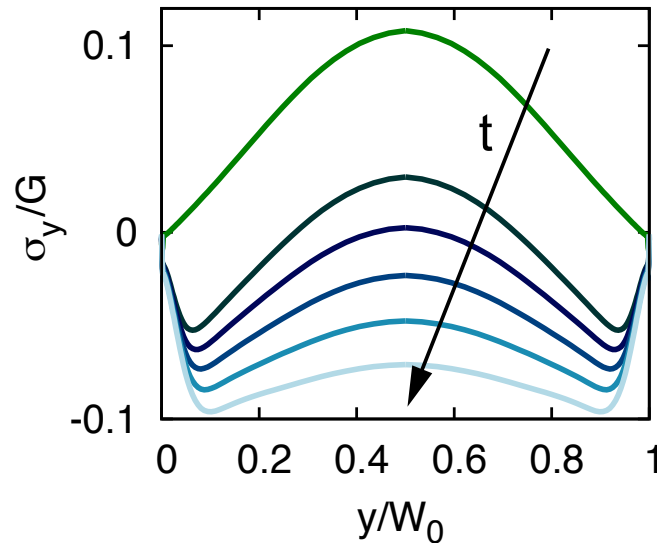
Swelling-induced wrinkling of an elastomeric membrane

- ▶ A homogeneous free-standing elastomeric sheet is stretched between clamps
- ▶ The stretched sheet is swollen with oil contained in a dish below the elastomer
- ▶ Upon reaching a critical solvent uptake, wrinkling occurs



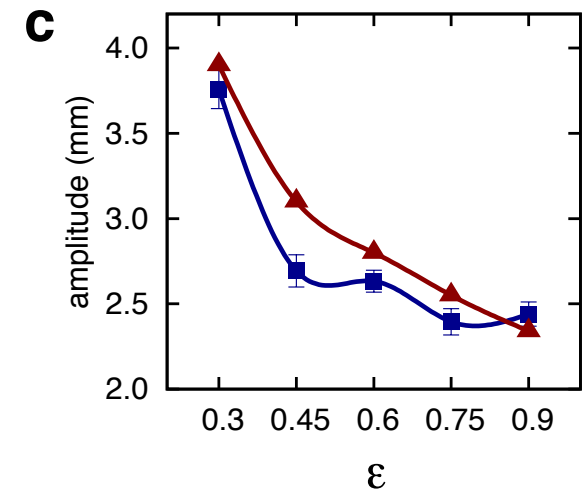
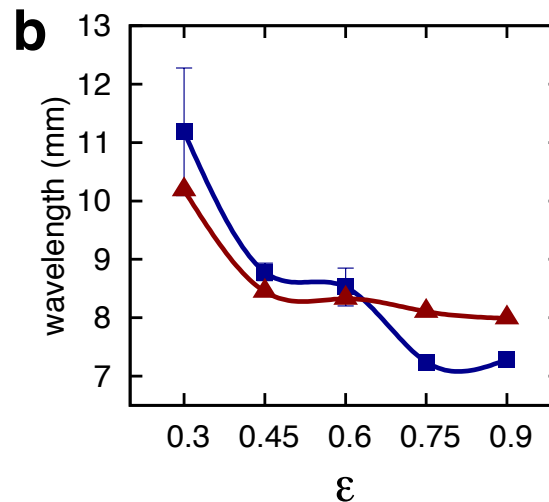
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Stretch-controlled wrinkling of an elastomeric membrane



- The membrane swells laterally against the confinement due to the clamps and the Poisson effect; as a result, the *transverse stress becomes negative*, thus triggering the instability

- **Wavelength and amplitude** of the wrinkles at equilibrium *decrease with an increasing applied strain*



Modeling of *smart* membranes - Balance equations

Kinematics: membrane with thickness microstructure (swelling material surface)

$\mathbf{v}_s = \dot{\mathbf{u}}_s$: surface velocity

$\eta = \dot{\delta}$: thickness stretch rate

$\hat{\mathbf{F}} = \mathbf{P}^T + \nabla_s \mathbf{u}_s$, $\mathbf{F}_s = \mathbf{P}_t \hat{\mathbf{F}}$: surface deformation gradients

\mathbf{P}, \mathbf{P}_t : projectors to the reference and current tangent space of the surface

Principle of Virtual Power $\mathcal{P}_b \subset \mathcal{S}, \forall \tilde{\mathbf{v}}_s, \tilde{\eta}$

$$\int_{\mathcal{P}_b} (\mathbf{S}_s \cdot \nabla_s \tilde{\mathbf{v}}_s + \sigma_n \tilde{\eta}) = \int_{\partial \mathcal{P}_b} \mathbf{t}_s \cdot \tilde{\mathbf{v}}_s + \int_{\mathcal{P}_b} (\mathbf{f}_s \cdot \tilde{\mathbf{v}}_s + c_n \tilde{\eta})$$

\mathbf{S}_s : surface stress

σ_n : thickness stress

\mathbf{t}_s : contact force

\mathbf{f}_s : distributed surface load

c_n : distributed thickness load

A.L., L. Teresi, A. DeSimone, *Continuum theory of swelling material surfaces with applications to thermo-responsive gel membranes and surface mass transport*, under review.

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$$\begin{aligned} \operatorname{div}_s \mathbf{S}_s + \mathbf{f}_s &= \mathbf{0}, & \text{on } \mathcal{S} \times \mathcal{I}, \\ \mathbf{t}_s &= \mathbf{S}_s \mathbf{m}_s, & \text{on } \partial \mathcal{S} \times \mathcal{I}, \\ \sigma_n &= c_n, & \text{on } \mathcal{S} \times \mathcal{I}. \end{aligned}$$

Balance of solvent mass

$$\frac{d}{dt} \int_{\mathcal{P}_b} c_s = - \int_{\partial \mathcal{P}_b} \mathbf{h}_s \cdot \mathbf{m}_s + \int_{\mathcal{P}_b} q_s$$

c_s : surface solvent concentration

\mathbf{h}_s : solvent flux

q_s : solvent mass source

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Free energy inequality

Coleman-Noll procedure

$$\frac{d}{dt} \int_{\mathcal{P}_b} \psi_s \leq \int_{\mathcal{P}_b} \mathbf{f}_s \cdot \dot{\mathbf{u}}_s + \int_{\partial \mathcal{P}_b} \mathbf{t}_s \cdot \dot{\mathbf{u}}_s + \int_{\mathcal{P}_b} c_n \dot{\delta} - \int_{\partial \mathcal{P}_b} \mu_s \mathbf{h}_s \cdot \mathbf{m}_s + \int_{\mathcal{P}_b} \mu_s q_s$$

μ_s : solvent chemical potential

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Helmholtz free energy (Flory-Rehner like)

$$\psi_s(\mathbf{F}_s, c_s) = \frac{1}{2} G_s h (\mathbf{F}_s \cdot \mathbf{F}_s + \delta^2 - 3) + g(c_s; T) - p_s (J_s \delta - 1 - \Omega_s c_s)$$

Elastic energy (Neo-Hooke)

G_s : network shear modulus

h : membrane ref thickness

\mathbf{F}_s : surface def gradient

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G_s : network shear modulus

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Mixing energy

T : temperature

Free energy inequality

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G_s : network shear modulus

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Mixing energy

T : temperature

Swelling constraint

$$J_s \delta = 1 + \Omega_s c_s$$

p_s : Lagrange multiplier (pressure)

$J_s = \det \mathbf{F}_s$: Area change

$$\Omega_s = \Omega / h$$

Ω : solvent molar volume

Free energy inequality

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Mixing energy

T : temperature

An increase in temperature leads to a reduction in chemical affinity between solvent and polymer, which hampers swelling.

Free energy inequality

Coleman-Noll procedure

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Constitutive equations

$$\mathbf{S}_s = \frac{\partial \psi_s}{\partial \hat{\mathbf{F}}} - p_s \delta \mathbf{P}_t^T \mathbf{F}_s^*,$$

$$\sigma_n = \frac{\partial \psi_s}{\partial \delta} - p_s J_s,$$

$$\mu_s = \frac{\partial \psi_s}{\partial c_s} + p_s \Omega_s,$$

$$\mathbf{h}_s(\hat{\mathbf{F}}, c_s, \nabla_s \mu_s) \cdot \nabla_s \mu_s \leq 0.$$

A.L., L. Teresi, A. DeSimone, *Continuum theory of swelling material surfaces with applications to thermo-responsive gel membranes and surface mass transport*, under review.

3D theory of swelling - Governing equations

► Balance of forces

$$\begin{aligned}\operatorname{div} \mathbf{S} + \mathbf{f} &= \mathbf{0}, & \text{on } \mathcal{B} \times \mathcal{I}, \\ \mathbf{t} &= \mathbf{S} \mathbf{m}, & \text{on } \partial \mathcal{B} \times \mathcal{I}.\end{aligned}$$

► Balance of solvent

$$\begin{aligned}\dot{c} &= -\operatorname{div} \mathbf{h}, & \text{on } \mathcal{B} \times \mathcal{I}, \\ -\mathbf{h} \cdot \mathbf{m} &= q & \text{on } \partial \mathcal{B} \times \mathcal{I}.\end{aligned}$$

► Swelling constraint

$$J = \det \mathbf{F} = 1 + \Omega c$$

► Constitutive equations

$$\mathbf{S} = \frac{\partial \psi}{\partial \mathbf{F}} - p \mathbf{F}^*,$$

$$\mu = \frac{\partial \psi}{\partial c} + p \Omega,$$

$$\mathbf{h}(\mathbf{F}, c, \nabla \mu) \cdot \nabla \mu \leq 0.$$

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$$\mathbf{h}(\mathbf{F}, c, \nabla \mu) \cdot \nabla \mu \leq 0.$$

Couplings with the boundary membrane $\mathcal{S} \subset \partial \mathcal{B}$

$$\mathbf{f}_s = \mathbf{f}_e - \mathbf{t}$$

$$q_s = q_e - q$$

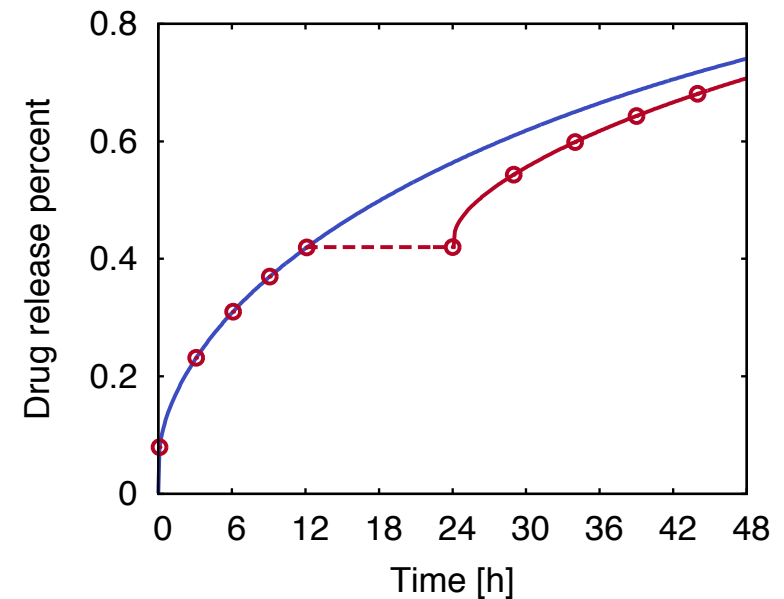
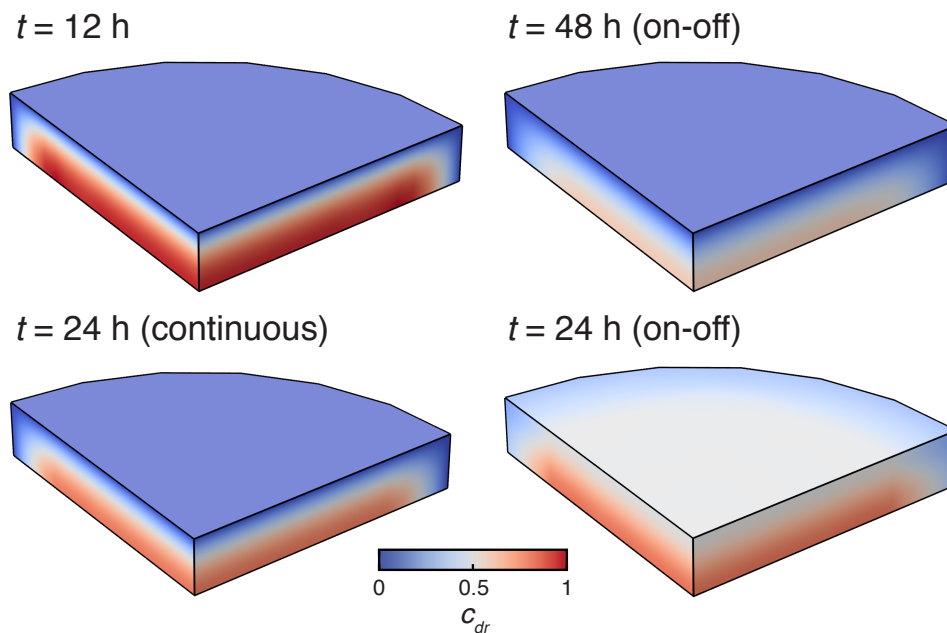
$$\mu = \mu_s$$

\mathbf{f}_e, q_e : External “loads”

A.L. et al., *Transient analysis of swelling-induced large deformations in polymer gels*, JMPS 61, 2013.

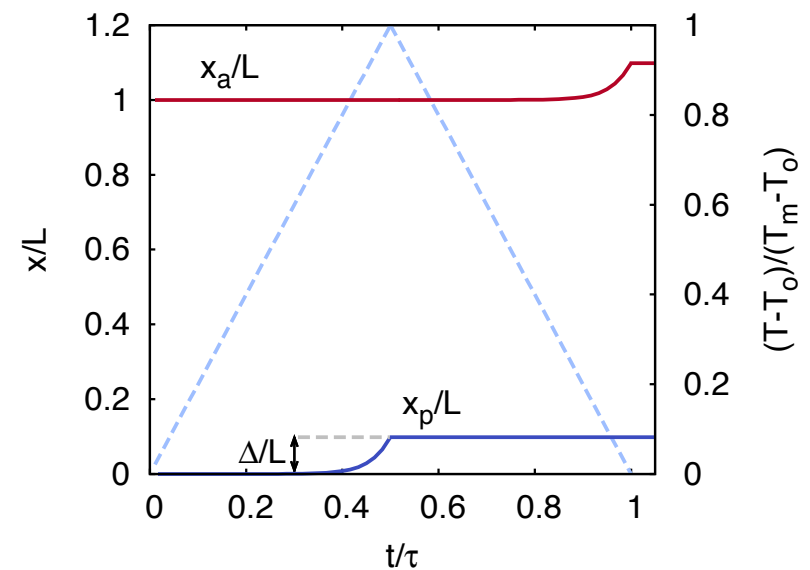
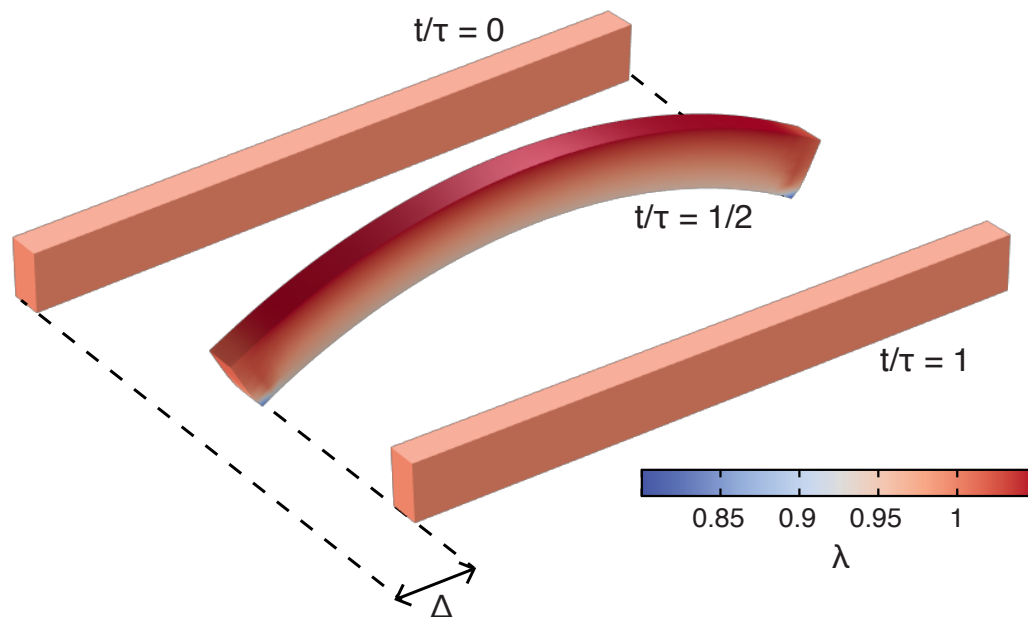
Smart drug delivery system

A hydrogel tablet coated with a thermo-responsive gel membrane. Drug loaded in the tablet is released by diffusion. When temperature is increased beyond the transition temperature, the coating gel shrinks, causing a reduction of the permeability of the surface, which hampers further drug release.



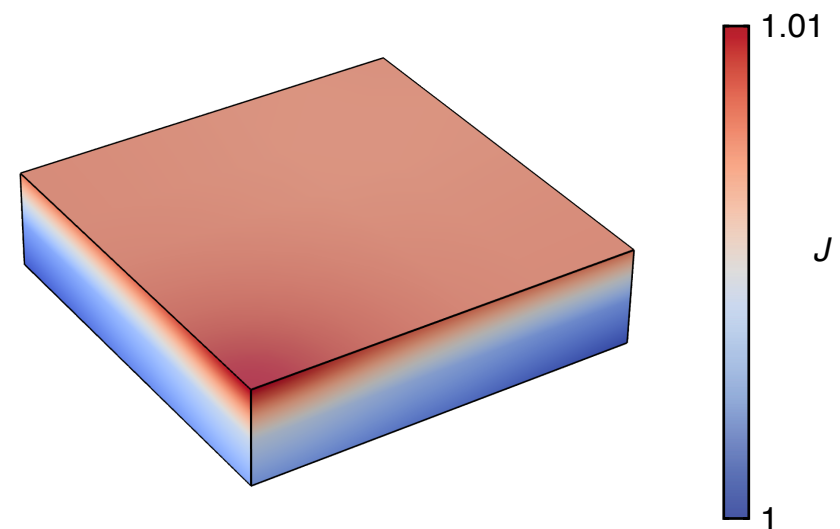
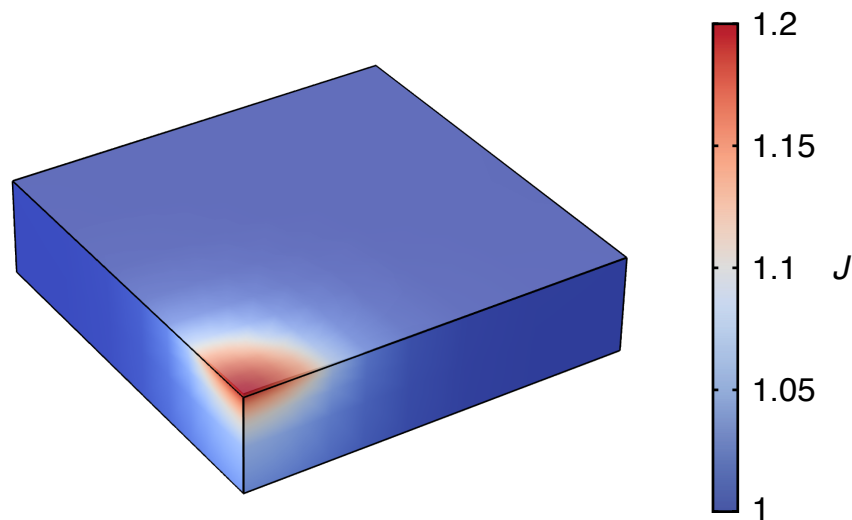
Temperature-activated crawler

A crawler advancing on a directional substrate by exploiting dry friction. When temperature is increased beyond the transition temperature, the crawler bends and the posterior edge in contact with the surface moves over it, while the anterior edge stays fixed.



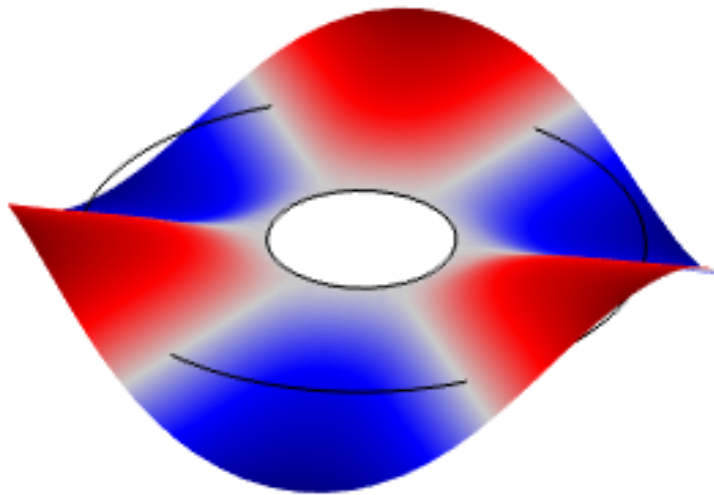
Spreading and absorption of a liquid on the surface of a gel layer

A gel layer coated with a surface having a different solvent permeability. A solvent flux is prescribed for 1 s in a circular region at the center of the layer. The solvent partially spreads over the surface and is also absorbed by the layer. Plot of the swelling ratio J at time $t = 1$ s over 1/4 of the gel layer for (left) $D_s = 1 \times 10^{-10} \text{ m}^2/\text{s} = D$ and for (right) $D_s = 1 \times 10^{-7} \text{ m}^2/\text{s}$.

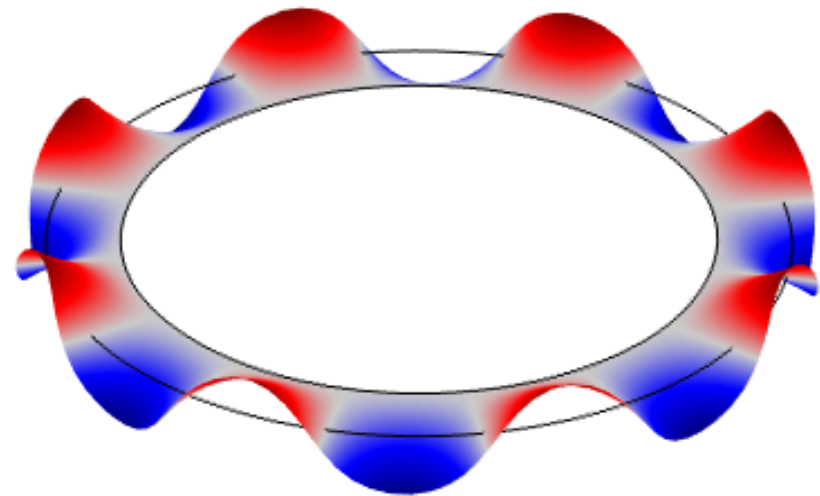


Wrinkling of a corona gel

A corona gel is clamped on its inner edge and swollen with a solvent. Compressive stresses arise due to the constraint and a wrinkling pattern emerges. Consistent with experiments, the wavenumber of the wrinkles increases with the ratio R_i/H between the inner radius of the annulus and the thickness of the membrane (the ratio R_o/H between the outer radius and the thickness is fixed).



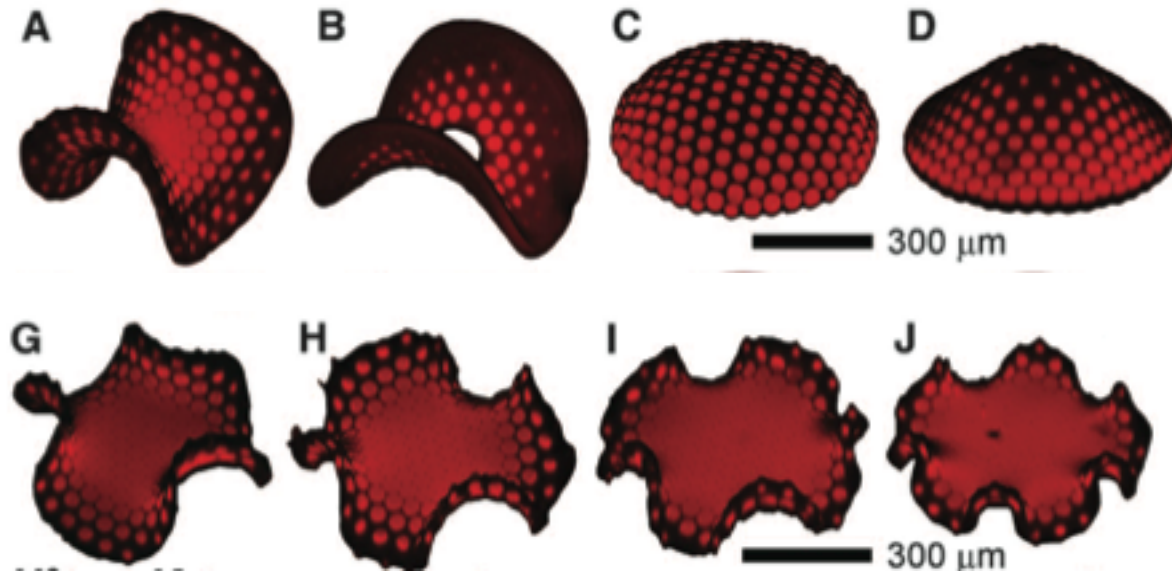
$$R_i/H = 8$$



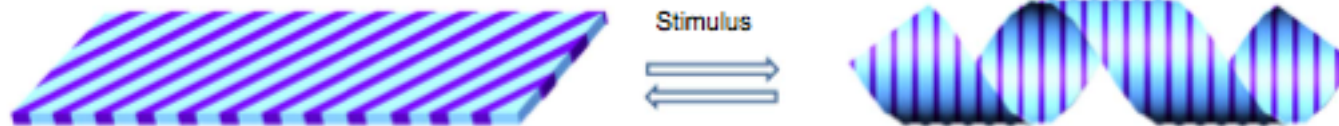
$$R_i/H = 12$$

Modeling of swelling shells for shape morphing

Morphing of 3D shapes starting from non-homogeneous swelling polymer sheets



(from Kim et al. 2012)



(from Wu et al. 2013)

- ▶ **Instability patterns** in soft materials are common in both natural and synthetic systems → applications harnessing instabilities
- ▶ **Shape morphing** applications involve 3D transformations of *soft/smart/swelling membranes*
- ▶ **Controlled wrinkling** of a *single-layer swelling membrane* may be achieved by tuning the **pre-stretch**
- ▶ A **swelling polymer gel membrane theory with thickness microstructure** can describe *boundary spreading/absorption* and *temperature-activated bending* in polymer gels