

Dynamics of super-absorbent hydrogels

Joseph Webber *and* Grae Worster

DAMTP Friday Fluids, 27 May 2022



Natural
Environment
Research Council

What are hydrogels?

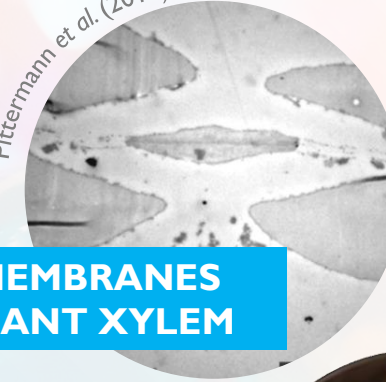
- Hydrophilic polymer scaffold surrounded by adsorbed water molecules.
- Can swell to hundreds of times their initial, dry, volume upon the introduction of water.
- Behave like elastic solids when swollen to a given degree, but also are permeable to the flow of water through interstices.

Increasing time left in water



Pittermann et al. (2010)

PIT MEMBRANES
IN PLANT XYLEM



ABSORBENT
NAPPY FILLING



Royal Horticultural Society

SOIL
IMPROVERS



CONTACT
LENSES



Existing modelling

General Theory of Three-Dimensional Consolidation*

MAURICE A. BIOT
Columbia University, New York, New York
(Received October 25, 1940)

The s
mechani
an elast
establish
properti
ments an
The ope
problem

Kinetics of swelling of gels

Toyochi Tanaka and David J. Fillmore

Department of Physics and Center for Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139
(Received 10 March 1978)

We present a theory of the kinetics of the swelling of a gel. The characteristic time of swelling is proportional to the square of a linear dimension of the gel and is also proportional to the diffusion coefficient of the gel network, which is defined as $D = E/f$ where E is the longitudinal bulk modulus of the network, and f is the coefficient of friction between the network and the gel fluid. This constitutes an essential difference between the present theory and the previous theory which is based on the assumption that the swelling time is determined by the diffusion coefficient of the fluid molecules. Experimental data are shown for spheres of 5% polyacrylamide gels and are analyzed using the present theory. The value of the diffusion coefficient obtained from the macroscopic swelling experiments shows excellent agreement with that obtained microscopically using laser light scattering spectroscopy.

Statistical Mechanics of Cross-Linked Polymer Networks

I. Rubberlike Elasticity¹

PAUL J. FLORY AND JOHN REHNER, JR.
Chemical Division, Esso Laboratories, Standard Oil Development Company, Elizabeth, New Jersey

Statistical Mechanics of Cross-Linked Polymer Networks

II. Swelling

PAUL J. FLORY AND JOHN REHNER, JR.
Chemical Division, Esso Laboratories, Standard Oil Development Company, Elizabeth, New Jersey
(Received October 4, 1943)

The interaction of solvents with cross-linked network structures, such as occur in vulcanized rubber, is subjected to a statistical mechanical treatment based on the model and procedure presented in the preceding paper. The activity of the solvent is expressed as a function of its concentration in the swollen network, and of the degree of cross-linking. The maximum degree of swelling of the network in contact with the pure solvent is related to the degree of cross-linking. The heat of interaction of the solvent with the network can be calculated from the temperature coefficient of maximum swelling. The theory leads to the conclusion that the swelling capacity should be diminished by the application of an external stress. Furthermore, the modulus of elasticity should decrease inversely with the cube root of the swelling volume.

- Linear poroelastic models (*Biot, Tanaka & Fillmore, Doi, ...*) treat the gel as a porous medium which behaves like a linear elastic material.
- Water is driven through the gel by gradients in pore pressure (Darcy's law); this leads to swelling/drying.
- **Key problem:** can't represent large swelling strains.
- Nonlinear models (*Flory & Rehner, Bertrand, Kang & Huang, ...*) determine a free-energy density from a microscopic understanding of the material.
- **Key problems:** can't determine parameters easily, analytically intractable.

Linear-elastic-nonlinear-swelling (LENS) constitutive relation

Key idea: allow for nonlinearities in isotropic strains corresponding to swelling only – assume deviatoric ‘shearing’ strains are small and linearise around these. Denote the polymer (volume) fraction by ϕ .

$$\begin{aligned}
 \underline{\underline{\mathbf{e}}} &= \frac{1}{2} \left[\nabla \underline{\underline{\xi}} + (\nabla \underline{\underline{\xi}})^T \right] \\
 &= \left[1 - \left(\frac{\phi}{\phi_0} \right)^{1/n} \right] \underline{\underline{\mathbf{I}}} + \underline{\underline{\boldsymbol{\epsilon}}}
 \end{aligned}$$

Displacement vector field \downarrow $(\nabla \underline{\underline{\xi}})^T$
Number of dimensions \leftarrow $1/n$
Fully-swollen equilibrium polymer fraction \uparrow ϕ_0
Pervadic pressure \downarrow p
Osmotic pressure \uparrow $\Pi(\phi)$
Shear modulus \downarrow $2\mu_s(\phi)$
| ϵ_{ij} | \ll 1 $\forall (i, j)$ \uparrow $\underline{\underline{\boldsymbol{\epsilon}}}$

$$\underline{\underline{\boldsymbol{\sigma}}} = - [p + \Pi(\phi)] \underline{\underline{\mathbf{I}}} + 2\mu_s(\phi) \underline{\underline{\boldsymbol{\epsilon}}}$$

Linear-elastic-nonlinear-swelling (LENS) dynamics

$$\frac{\partial \phi}{\partial t} + \nabla \cdot (\phi \mathbf{u}_p) = 0$$

$$\frac{\partial}{\partial t} (1 - \phi) + \nabla \cdot [(1 - \phi) \mathbf{u}_w] = 0$$

Polymer and water conservation

$$\underline{\underline{\sigma}} = -[p + \Pi(\phi)] \underline{\underline{\mathbf{I}}} + 2\mu_s(\phi) \underline{\underline{\epsilon}}$$

$$\nabla \cdot \underline{\underline{\sigma}} = 0$$

Cauchy's momentum equation

$$\mathbf{u} = (1 - \phi) (\mathbf{u}_w - \mathbf{u}_p) = -\frac{k(\phi)}{\mu_l} \nabla p$$

Darcy's law

$$\frac{\partial \phi}{\partial t} + \cancel{\mathbf{q} \cdot \nabla \phi} = \nabla \cdot \left[\frac{\phi k(\phi)}{\mu_l} \nabla \left\{ \Pi(\phi) + 2(n-1)\mu_s(\phi) \left(\frac{\phi}{\phi_0} \right)^{1/n} \right\} \right]$$

due to small deviatoric strains
(low Péclet number limit)

A conceptual rheometer

- The gel constitutive and dynamic model introduced here depends on only three material parameters, all of which are measurable macroscopically:

$$\Pi(\phi)$$

Osmotic pressure

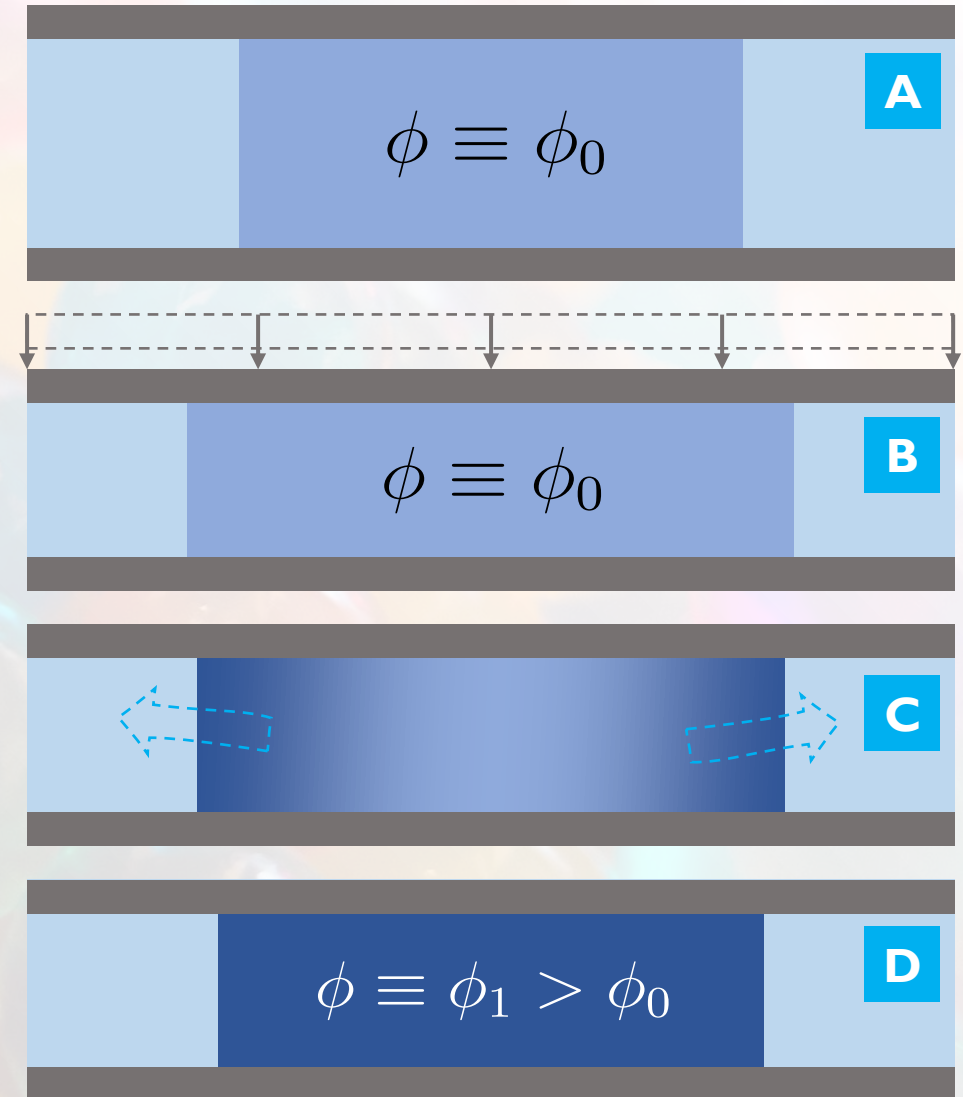
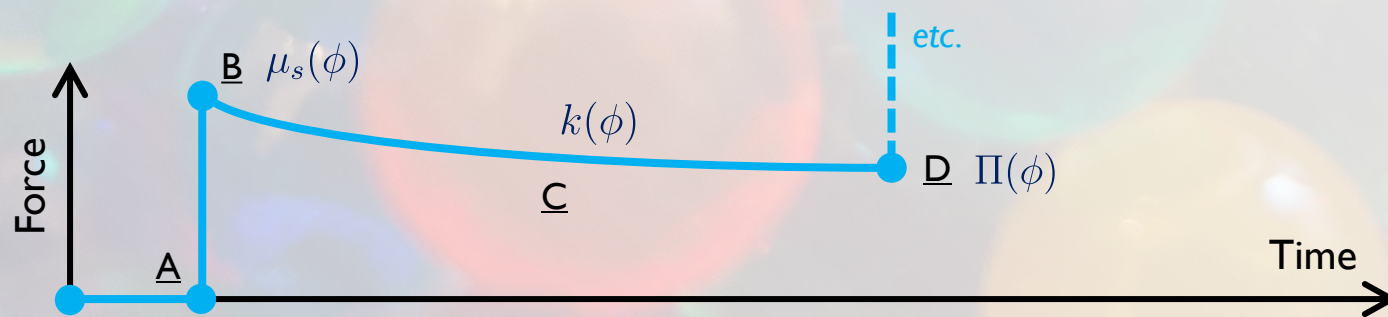
$$\mu_s(\phi)$$

Shear modulus

$$k(\phi)$$

Permeability

- Constitutive relations for all three of these parameters can be derived from a single experiment, placing a layer of gel in water and stepping its height down incrementally, then measuring the force on the top plate.

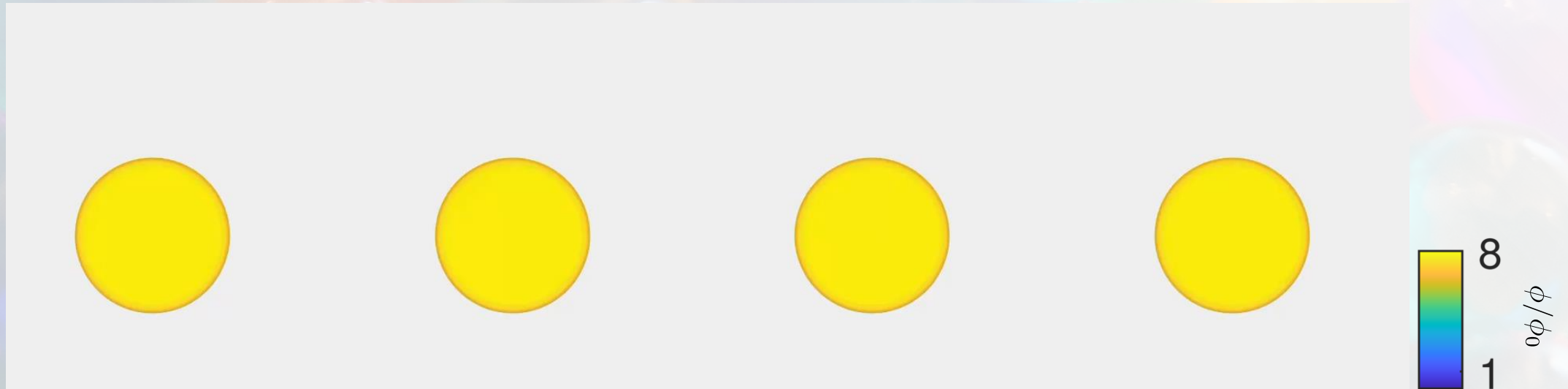


Swelling of a gel bead

- Boundary conditions supply a (time-varying) interfacial polymer fraction and water is drawn in diffusively, as shown below, approaching a steady state where the entire gel is fully-swollen.

$$\sigma_{rr}|_{r=a(t)} = 0 \quad \text{so} \quad \Pi(\phi_1) = 4\mu_s(\phi_1) \left[\frac{a_0}{a(t)} - \left(\frac{\phi_1}{\phi_0} \right)^{1/3} \right]$$

- Can swell or dry to a large degree (significant isotropic strains) without introducing large deviatoric strains, since variation in polymer fraction along a radial transect is small at all times.



Displacement formulation

- Most simple problems considered in the literature use polymer conservation to set the size and shape of a gel; can't do this for more complicated shapes.
- Linear elasticity: displacement field satisfies biharmonic equation. We can find an analogue here forced by polymer fraction field.

$$\nabla^4 \xi = -n \nabla \nabla^2 \left(\frac{\phi}{\phi_0} \right)^{1/n}$$

EXAMPLE: drying of cylinders (from top only)

$$\xi = \left[1 - (\phi/\phi_0)^{1/3} \right] r$$

$$\zeta = \int_0^z 1 - (\phi/\phi_0)^{1/3} dz' + \frac{r^2}{2} \frac{\partial}{\partial z} \left(\frac{\phi}{\phi_0} \right)^{1/3}$$

As a consequence of small deviatoric strains, isotropic swelling dominates the displacement field.

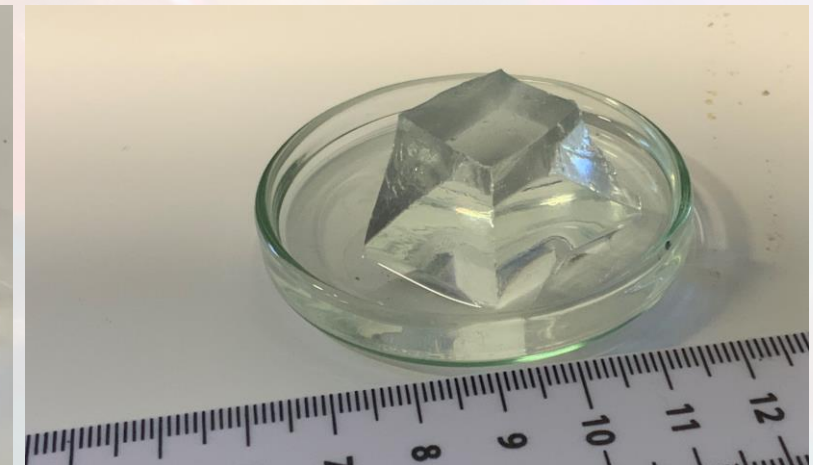
Differential swelling leads to curved interfaces.

More drying



Concave top

Convex base



- Most simple problems consider gel; can't do this for more complex
- Linear elasticity: displacement field, polymer fraction field.

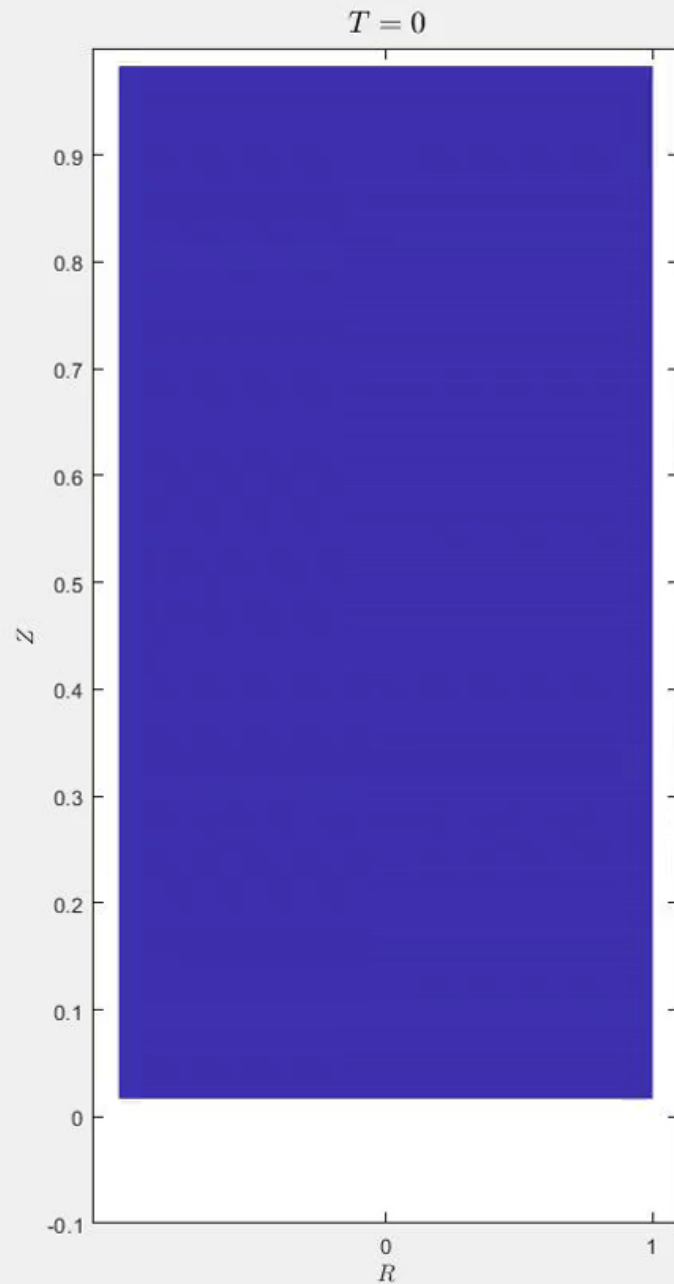
EXAMPLE: drying of cylinders

$$\xi = \left[1 - (\phi/\phi_0)^{1/3} \right] r$$

$$\zeta = \int_0^z \left[1 - (\phi/\phi_0)^{1/3} \right] dz' + \frac{r^2}{2} \frac{\partial}{\partial z} \left(\frac{\phi}{\phi_0} \right)$$

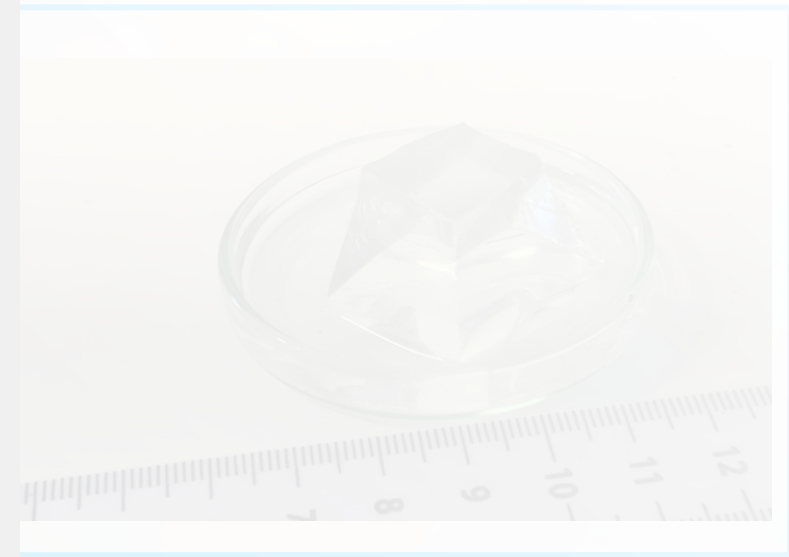
As a consequence of small deviatoric isotropic swelling dominates the displacement field.

Differential swelling leads to curved



element formulation

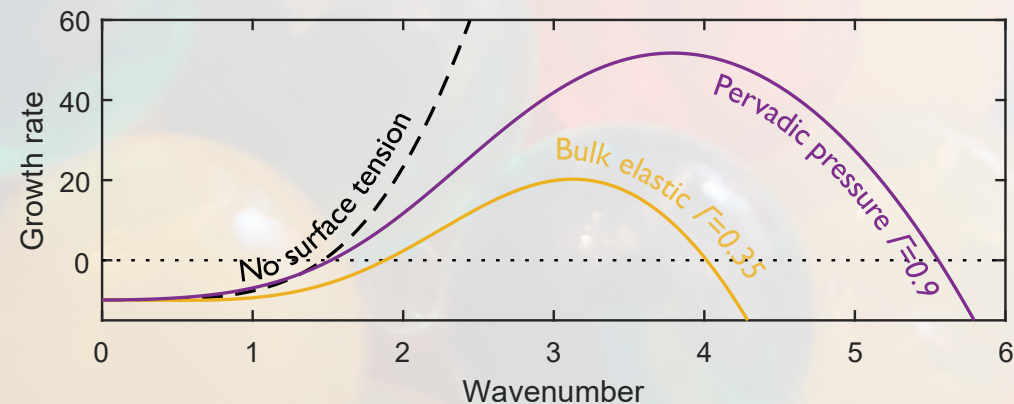
... to set the size and shape of a
... and an analogue here forced by



Wrinkling instabilities



- As seen in the confined swelling problem, a gel swells from the outside in, with a more swollen surface layer increasing diffusively in thickness as more water is drawn into the polymer scaffold.
- The greater degree of swelling in the surface layer creates a lateral compressive strain, which leads to compressive stresses, relieved by the formation of wrinkles.
- Ultraviolet catastrophe in the growth rates; introduce surface tension to resolve this (but how?)



Conclusions and future work

- A linear-elastic-nonlinear-swelling theory allows us to capture the key behaviour of large-swelling hydrogels in a model which is analytically-tractable and based on only three macroscopically-measurable material parameters.
- This theory can be applied to explain a wide range of phenomena seen when gels swell or dry (swelling of spheres, drying of cylinders, wrinkling of gel-water interfaces).
- Can we pin down the mechanism behind water-gel surface tension; can qualitatively different wrinkling patterns allow us to distinguish between a surface tension arising from discontinuities in elastic stress or pervadic pressure?
- Can then apply our understanding of hydrogels to a potentially-important natural problem – the ascent of water in tall trees. Hydrogels are found in the pit membranes between xylem vessels; can discontinuities in p help avoid the significant negative pressures of cohesion-tension theory?