

# Dynamics of super-absorbent hydrogels

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The current understanding of transport of water in plants **relies on significant negative pressures<sup>1</sup>** in the xylem to draw water up against gravity.

We expect such pressures to **lead to cavitation, spontaneous boiling, and xylem collapse<sup>2</sup>**, especially in plants subjected to water stress.

The pit membranes separating one xylem vessel from another both constrict flow but also **contain hydrogels formed from organic polymers and water<sup>3</sup>**. These can be modelled using our new approach.

We propose a contribution from **discontinuities in the liquid pressure arising at the interface** between hydrogel and water in pits between xylem cells.

## The negative pressure problem



Assuming a steady evaporation flow rate, there must be a pressure difference in the water of the xylem in a tree which balances the hydrostatic pressure, in order to drive flow against gravity. Order-of-magnitude scalings can be used to deduce a representative pressure drop required in a tree to produce such a flow.

$$\Delta p = \rho g \Delta h \approx 100 \text{ kPa}$$

Gravitational acceleration  $\sim 10 \text{ m s}^{-2}$   
Water density  $\sim 10^3 \text{ kg m}^{-3}$   
Height change  $\sim 10 \text{ m}$

This rises to around 2 MPa if the effects of friction in the xylem are factored in<sup>2</sup>, suggesting water at the top of a tree will be at pressures of -1 to -4 MPa relative to the atmosphere.

At pressures of around -0.1 MPa, water spontaneously boils and we expect cavitation, collapse of xylem vessels and damage to the tree. Though some authors claim to have measured such pressures<sup>4,5</sup>, they are difficult to reproduce even in laboratory environments without cavitation. This motivates seeking an additional driving mechanism in the transport of fluid, in addition to classical cohesion-tension theory.

## Linear-elastic-nonlinear-swelling gels

Hydrogels comprise hydrophilic polymer chains (of volume fraction  $\phi$ ) surrounded by adsorbed water. In many cases, the polymer volume percentage may be as small as 1%<sup>7</sup>. Modelling of hydrogels needs to couple an understanding of the gel as an elastic material with its porous nature, and therefore is a key problem in poroelasticity. Existing models can be grouped into two main approaches:

- **Fully-nonlinear models<sup>7</sup>** use a microscopic understanding<sup>8,9</sup> of polymer and water molecule interactions to describe the macroscopic behaviour of the gel.
  - + **Accurately models gels under large strains due to swelling and drying**
  - **Relies on a complicated chemical understanding of water-polymer interactions with parameters that are hard to measure macroscopically.**
- **Fully-linear models<sup>10</sup>** use linear poroelasticity to relate the stresses and strains on a gel, with Darcy's law used to describe the flow of water.
  - + **Describes any given gel using only macroscopic parameters which are easy to measure, and separates out fluid flow from elasticity.**
  - **Linear elasticity is invalid for large strains<sup>11</sup> – hydrogels may swell with isotropic swelling strains of much greater than 100%.**

In our *linear-elastic-nonlinear-swelling* model, we allow for nonlinearities in the (potentially large) isotropic strains corresponding to the swelling and drying of gels whilst linearising around deviatoric strains corresponding to shearing deformation. In effect, a hydrogel swollen to any given degree is treated as an instantaneously incompressible linear-elastic material.

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

STRESS TENSOR

### PRESSURE

In a two-component system we separate the bulk pressure  $P$  into two parts<sup>12</sup>:

- A pervadic pressure  $p$  which is the pressure of the liquid phase as measured by a transducer, separated from the gel by a partially permeable membrane.
- An osmotic pressure  $\Pi$  dependent only on polymer fraction. This can be viewed as the pressure which must be applied to prevent the uptake of water by a gel, where hydrophilic polymer chains attract water molecules.

### SHEAR MODULUS

Measures resistance to shear deformation, and depends on degree of swelling

### DEVIATORIC STRAIN

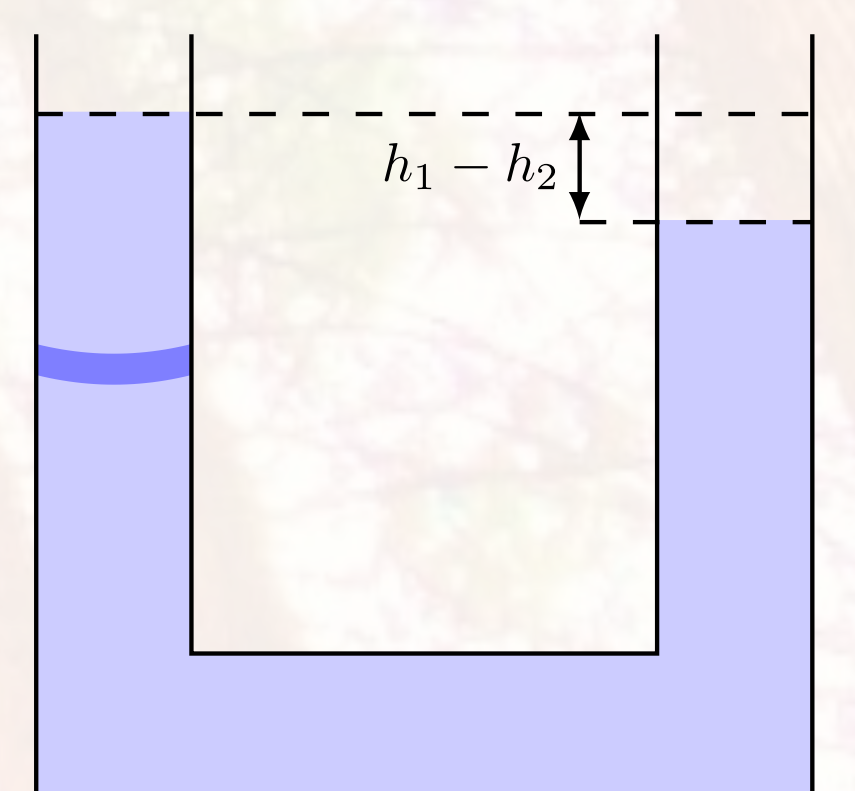
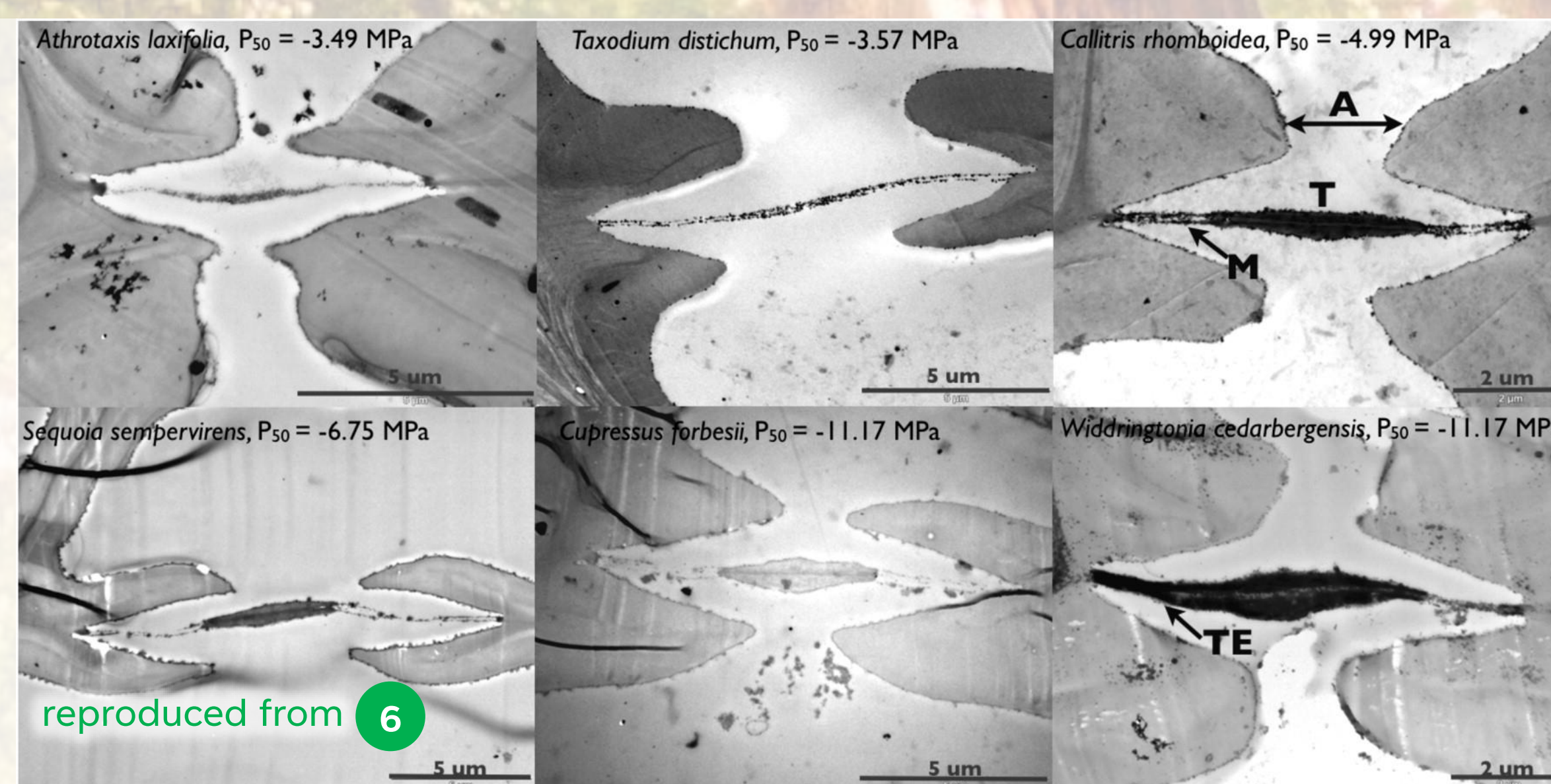
Strain can be separated into an isotropic part due to swelling and drying (changes in polymer fraction) and a part due to deviatoric deformation,  $\epsilon$ . The key assumption of our model is that  $\epsilon$  is small.



## Pits and bordered pits

In between adjacent cells comprising the xylem of vascular plants lie pits, which permit the transport of sap laterally in addition to the vertical transport which occurs through the hollow lumen. These pits comprise a permeable membrane spanning a small gap of around 1-10  $\mu\text{m}$  in diameter, with examples shown in cross-section in the first two images<sup>6</sup> on the right. In some conifer species the pit structure is more complicated, forming a so-called **bordered pit**. Here, as shown in the final four images of the figure, a solid **torus** structure (labelled T) is held in place by a flexible and permeable elastic **margo** (M) which surrounds it and deforms in response to pressure and flow.

These elastic pit structures comprise organic polymers surrounded by water, and some authors have suggested that the resulting hydrogel could play an important role in the transport of fluid in plants<sup>3</sup>. They are able to bend as a circular membrane, swell and dry<sup>3</sup>.



In this U-tube experiment, the equilibrium height of fluid in the arm of the tube containing the gel membrane is higher than in the other arm owing to the surface tension effect at the interface between curved gel and water.

## Swelling and drying of hydrogels

The dynamics of gels can be understood as being driven by the flow of water throughout. The interstitial velocity of water is given by Darcy's law:

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

Permeability  $k(\phi)$   
Viscosity  $\mu_l$

When coupled with Cauchy's momentum equation, it becomes possible to derive a nonlinear diffusion equation governing the polymer fraction  $\phi$  as a gel swells or dries,

$$\frac{\partial \phi}{\partial t} = \nabla \cdot \left[ \frac{\phi k(\phi)}{\mu_l} \left\{ \frac{\partial \Pi}{\partial \phi} \nabla \phi + 4\mu_s(\phi) \nabla \left( \frac{\phi}{\phi_0} \right)^{1/3} \right\} \right]$$

Involving only a handful of material parameters of a gel:

- **The osmotic pressure** and how it relates to polymer fraction.
- **The permeability**
- **The shear modulus**
- **The equilibrium polymer fraction**  $\phi_0$ , which is the polymer fraction reached by a given hydrogel if placed in water and allowed to swell with no constraints<sup>10</sup>. This depends on temperature and can be as low as  $10^{-2}$  for some gels.

In addition, the shape of the hydrogel can be deduced from the forced biharmonic equation describing the displacement  $\xi$  of any given point from its position at equilibrium:

$$\nabla^4 \xi = -3\nabla \nabla^2 \left( \frac{\phi}{\phi_0} \right)^{1/3}$$

## Gel membranes & surface tension

To apply our model to understand the flow of water through pit membranes in a plant cell, we start by considering a single thin circular membrane. Under a load  $Q$  per unit area, the vertical deflection  $\zeta$  of a circular linear-elastic membrane satisfies

$$\nabla^4 \zeta = -Q/D$$

for  $D$  the bending moment<sup>11</sup>. Thus, if we assume that the membrane has a constant curvature  $K$ , the curvature under a given load is set by

$$EK^3 = Q$$

At curved interfaces between gel and water, there is a discontinuity in the pervadic pressure arising from an effect akin to surface tension<sup>13</sup>. This can be quantified by the relation

$$\Delta p = \gamma \kappa$$

For a xylem pit<sup>13,6</sup>,  $\gamma \approx 10^{-2} \text{ N m}^{-1}$  whilst  $K \approx 10^5 \text{ m}^{-1}$   
Given by  $p^+ - p^-$ , akin to the Young-Laplace equation

Therefore, under a load which arises purely from hydrostatic pressures, there exists equilibrium solutions where

$$2\gamma \kappa = EK^3 \Rightarrow \kappa = 0, \pm \sqrt{\frac{2\gamma}{E}}$$

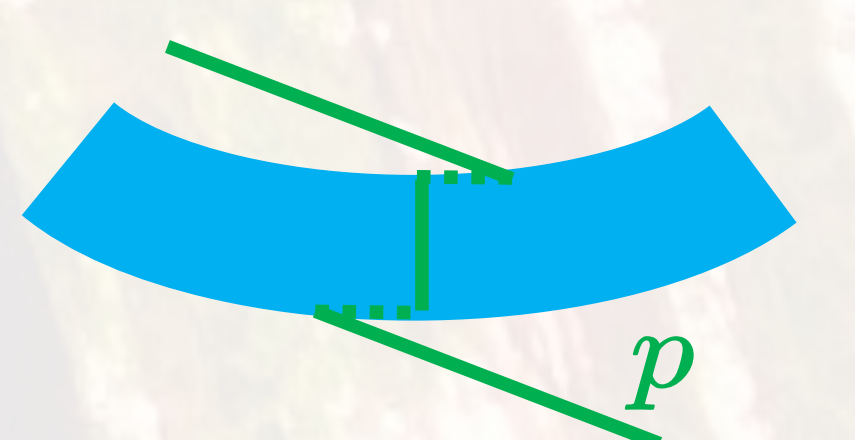
## A simple experiment

Consider a U-shaped tube with a circular gel membrane placed in the left-hand arm, with equilibrium water heights  $h_1$  and  $h_2$  on the left and right sides, respectively. Then, the pressure difference across the membrane is given by

$$\Delta p = \rho g(h_1 - h_2)$$

Which, for nonzero  $\gamma$ , admits an equilibrium solution where  $h_1 > h_2$  and thus a column of water is supported against gravity by the surface tension effect of the membrane.

$$h_1 - h_2 = \sqrt{\frac{2\gamma^3}{\rho^2 g^2 E}}$$



## Membranes in trees

As we have seen, a single hydrogel membrane can support a certain height of fluid against gravity due to discontinuities in the pervadic pressure across curved water-gel interfaces. If each bordered pit contains such a curved membrane, it is possible that water can be transported to great heights against gravity **without the need for significant negative pressures (relative to atmospheric pressure) at the top**. Each membrane need only contribute a small amount to the overall effect,  $2\gamma \Sigma \kappa_j$