Multidirectional gel swelling and drying

A linear-elastic-nonlinear-swelling theory for hydrogels

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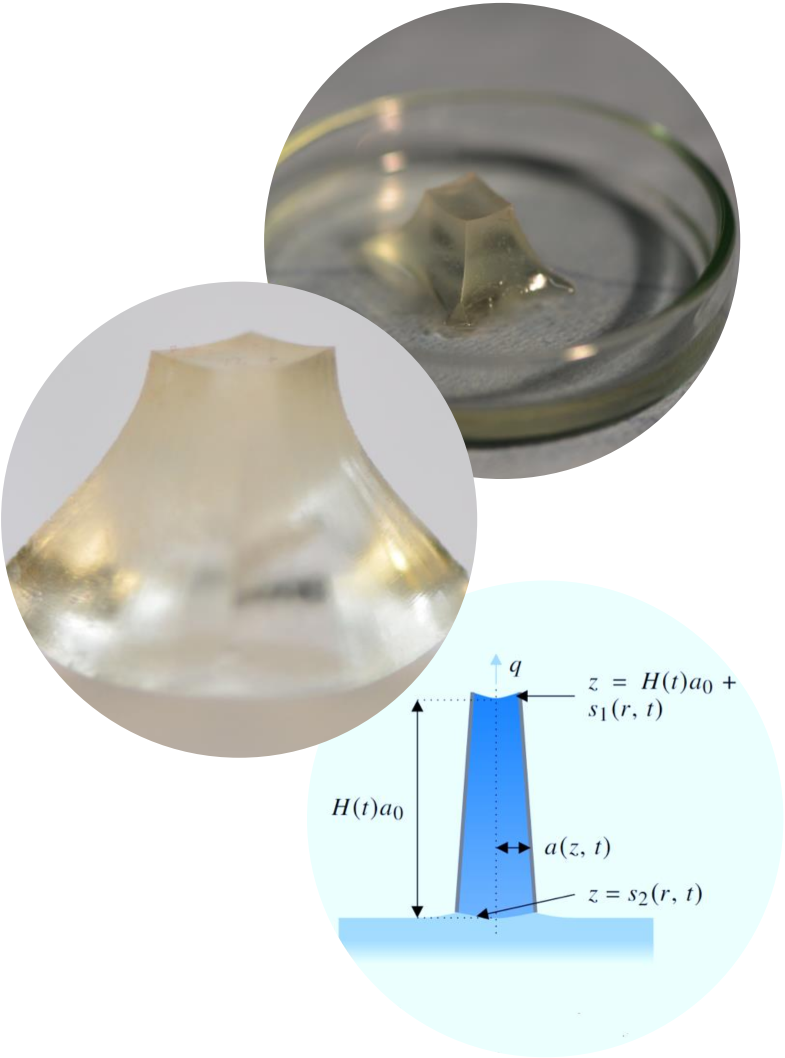

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Modelling super-absorbent polymers

- Super-absorbent polymers (SAPs) are characterised by polymer fractions often as small as 1% by volume at equilibrium.

- Therefore, large (>100%) swelling strains are involved in the transition from partially-dry to fully-swollen states.

LINEAR POROELASTICITY
Biot (1941), Doi (2009), Punter *et al.* (2020)

- Analytically-tractable; treats the gel as a linear-elastic material separating pore pressure from material elasticity.

- *But* linear elasticity is only valid for small strains – to describe large swelling this is inadequate.

NONLINEAR (FREE-ENERGY) APPROACH
Flory & Rehner (1943a,b), Bertrand (2016)

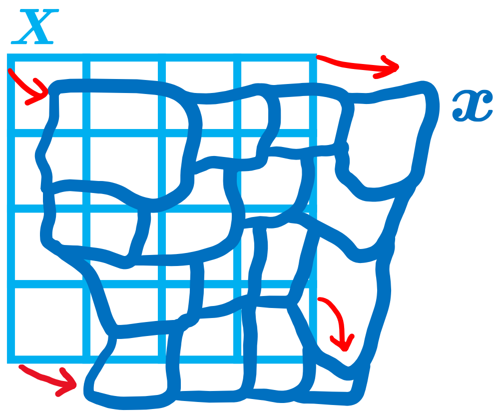
- Derive a free-energy density from a microscopic understanding of the material.

- *But* this requires an understanding of intermolecular interactions and doesn’t separate out the phases.

Image reproduced from Bertrand *et al.* (2016)

Linear-elastic-nonlinear-swelling theory

- Take the reference state for a gel to be the fully-swollen equilibrium, $\phi \equiv \phi_0$.
- Label gel elements in this state by Lagrangian coordinates $\boldsymbol{X}$ and introduce the displacement $\boldsymbol{\xi}(\boldsymbol{x}) = \boldsymbol{x} - \boldsymbol{X}$ to represent a deformation.



$$\mathbf{e} \equiv \frac{1}{2}\left[\boldsymbol{\nabla}\boldsymbol{\xi} + (\boldsymbol{\nabla}\boldsymbol{\xi})^{\mathrm{T}}\right]$$

$$\equiv \left[1 - \left(\frac{\phi}{\phi_0}\right)^{1/n}\right]\mathbf{I} + \epsilon$$

The key idea underpinning our model is that deviatoric strains are small and thus we have linear elasticity in all but swelling strain.

Volume changes correspond to changes in polymer fraction since $\det\left[\partial x_i / \partial X_j\right] = \phi_0/\phi$

The constitutive relation and pressure

- Treating the gel, when swollen to a certain degree, as a linear elastic material, the stress tensor is given by

$$\boldsymbol{\sigma} = -P\mathbf{I} + 2\mu_s\boldsymbol{\epsilon}$$

  where P is the bulk pressure and μ_s is the shear modulus.

- Allow for nonlinearities in polymer fraction, and therefore $\mu_s = \mu_s(\phi)$.

- Separate $P = p + \Pi$ into **pervadic pressure** p (Peppin et al. 2005) and osmotic pressure Π, where the former is the pressure as measured by a transducer separated from the liquid by a partially-permeable membrane.

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

$$= K(\phi)\frac{\phi - \phi_0}{\phi_0}$$

Gel dynamics

- Dynamics are governed by the flow of water through the gel structure, with interstitial flow described by Darcy's law, arising from gradients in pervadic pressure.

- We have three equations from which a governing equation for the change of polymer fraction in time can be derived:
  - Polymer conservation
  - Water conservation
  - Cauchy's momentum equation

Permeability

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

$\boldsymbol{q} = \phi \boldsymbol{u_p} + (1-\phi)\boldsymbol{u_l}$

advective term

We henceforth consider the low-Péclet number limit where diffusive behaviour dominates advection.

Boundary conditions and the shape of a gel

- In order to solve the equation we have derived, we need boundary conditions, usually at the interface between gel and air/water/other media:
  - Continuity of normal stress
  - Continuity of tangential stress
  - Fixed evaporative flux
  - Impermeable boundaries $\boldsymbol{n} \cdot \boldsymbol{\nabla} p = 0$

- However, we don't actually know the position of the boundary – in one-dimensional swelling problems, we can use polymer conservation. Need a different approach for general problems.

- Can we find the displacement field given polymer fraction? Not immediately, all we know is $\boldsymbol{\nabla} \cdot \boldsymbol{\xi} = n \left[1 - (\phi/\phi_0)^{1/n}\right]$.

- Recall in linear elasticity that $\nabla^4 \boldsymbol{\xi} = \mathbf{0}$ in the absence of any body force.

Boundary conditions and the shape of a gel

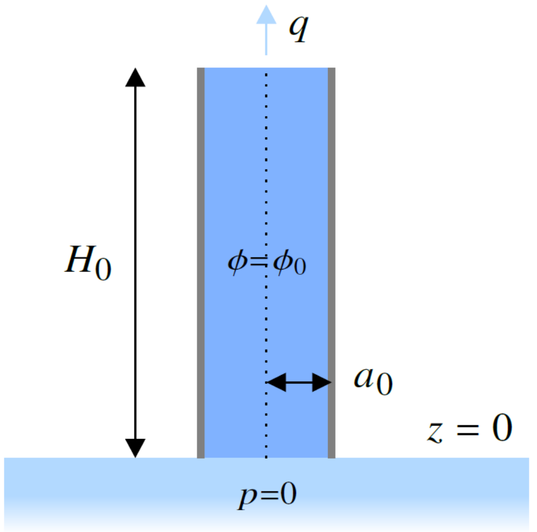
- In the case of the hydrogels we are considering, the assumption of small deviatoric strain alongside Cauchy's momentum equation in the absence of body forces implies that

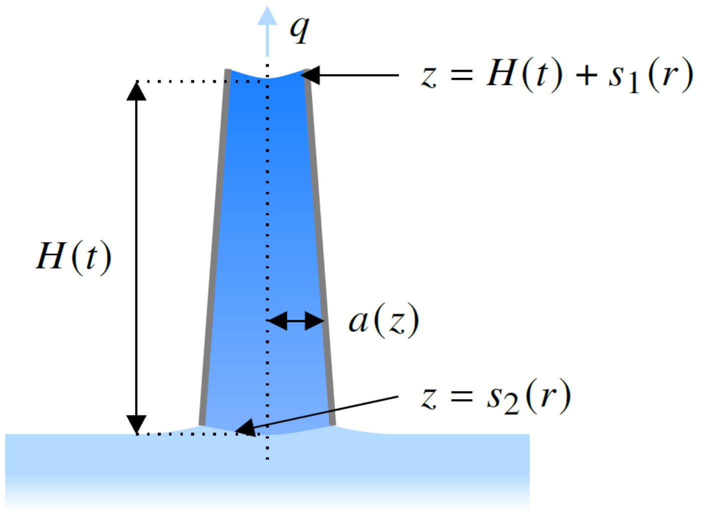
$$\nabla^4 \boldsymbol{\xi} = n \boldsymbol{\nabla} \nabla^2 \left(\frac{\phi}{\phi_0} \right)^{1/n}$$

- Physically, this can be interpreted as a forcing due to curvatures in surfaces of constant polymer fraction.

Drying of slender cylinders

- Physical setup: cylinder of height H_0 and radius a_0 drying from its top surface only through a fixed evaporation flux q.
- Experiments show the formation of a curved interface on the top and bottom – can our model describe this?
- Start with the assumption that $H_0/a_0 \gg 1$ and solve for the polymer fraction and shape.
- Slenderness implies that $\phi(r, z) = \phi(z)$
- Can determine polymer fraction – seek the displacement field $\boldsymbol{\xi} = \xi\hat{\boldsymbol{r}} + \zeta\hat{\boldsymbol{z}}$.





Drying of slender cylinders

$$\nabla^4\zeta = \frac{\partial^3}{\partial z^3}\left(\frac{\phi}{\phi_0}\right)^{1/3} = O(\varepsilon^2) \quad \text{so} \quad \zeta = A(z)r^2 + B(z) + O(\varepsilon^2)$$

$$\xi = \frac{1}{2}\left\{3\left[1-\left(\frac{\phi}{\phi_0}\right)^{1/3}\right] - \frac{\partial B}{\partial z}\right\}r - \frac{1}{4}\frac{\partial A}{\partial z}r^3$$ (arising from $\boldsymbol{\nabla}\cdot\boldsymbol{\xi} = \operatorname{tr}\mathbf{e}$)

Now require the deviatoric strain to be small, implying that

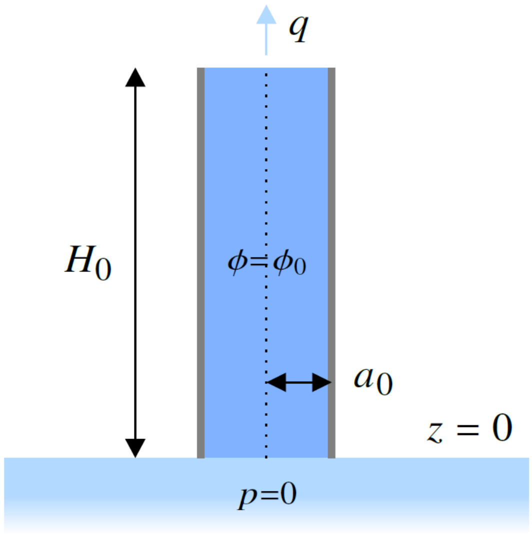
$$B(z) = \int_0^z 1 - (\phi/\phi_0)^{1/3}\,\mathrm{d}z' + C(z) \quad \text{with } C(0) = 0 \text{ and } \partial C/\partial z = O(\varepsilon).$$

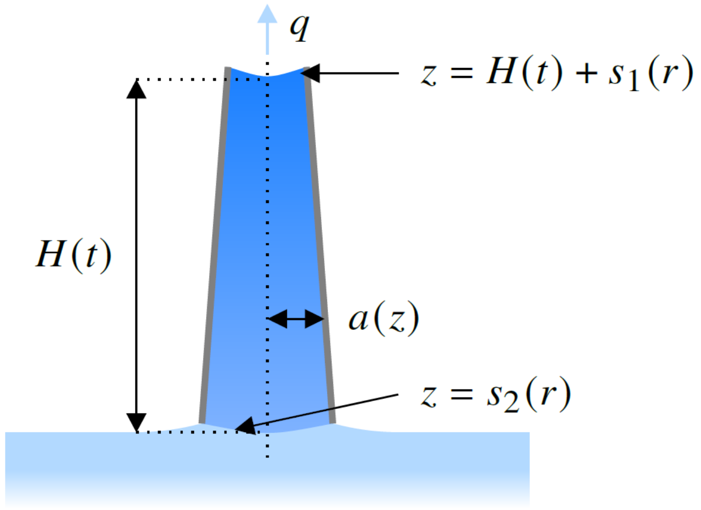
Zero tangential stress on the surface of the cylinder gives

$$A(z) = \frac{1}{2}\frac{\partial}{\partial z}\left(\frac{\phi}{\phi_0}\right)^{1/3}.$$

Calculate the bulk pressure field using Cauchy's momentum equation and impose zero normal stress on the surface to give

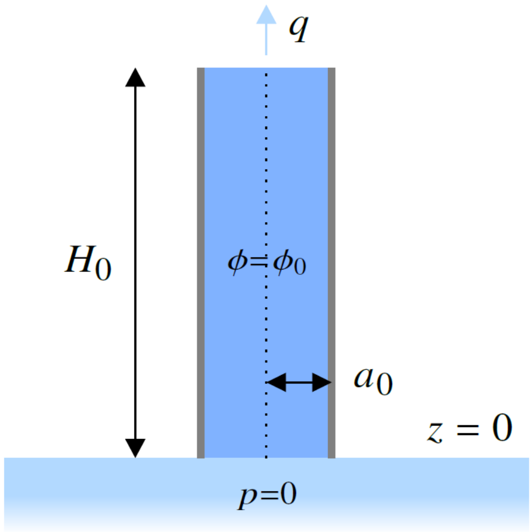
$$C(z) \equiv 0.$$





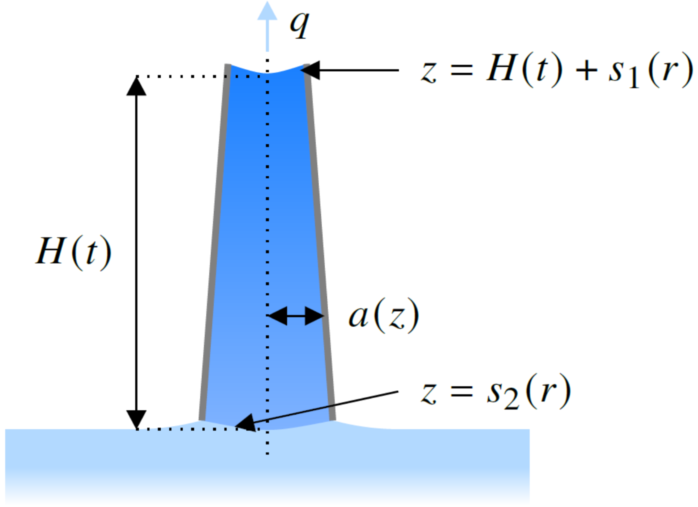
Drying of slender cylinders

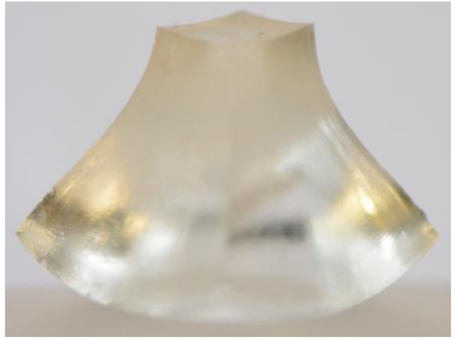
$$\left.\begin{aligned} \xi &= \left[1-(\phi/\phi_0)^{1/3}\right] r\,, \\ \zeta &= \int_0^z 1-(\phi/\phi_0)^{1/3}\,\mathrm{d}z' + \frac{1}{2}\frac{\partial}{\partial z}\left(\frac{\phi}{\phi_0}\right)^{1/3} r^2. \end{aligned}\right\} \quad \left\{\begin{aligned} a(z) &= (\phi/\phi_0)^{-1/3} a_0\,, \\ H_0 &= \int_0^{H(t)} (\phi/\phi_0)^{1/3}\,\mathrm{d}z'. \end{aligned}\right.$$

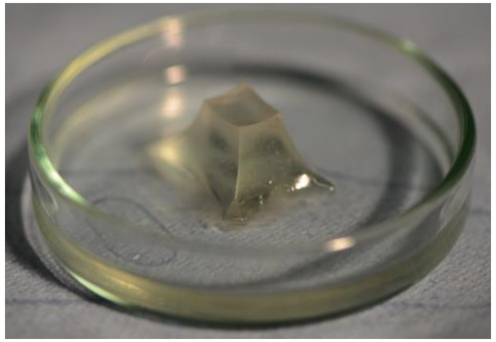


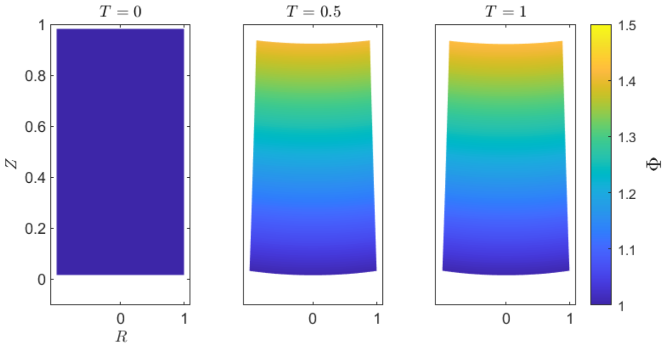
- Importantly, these results also show that the curvature of the top and bottom surfaces arises from gradients in polymer fraction.

- These results match those of experiments which show the formation of a convex base and concave top.







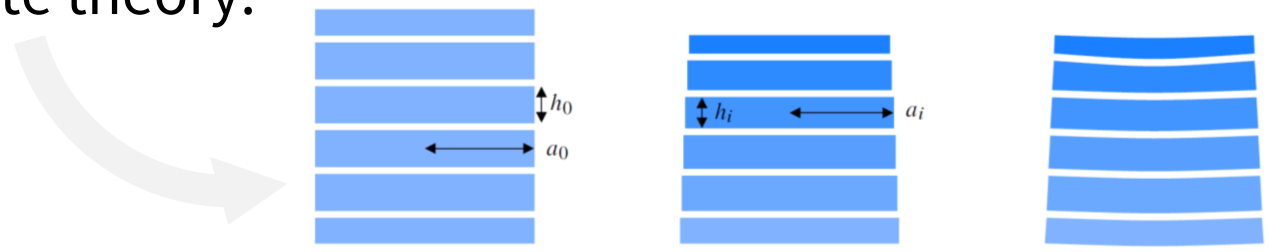


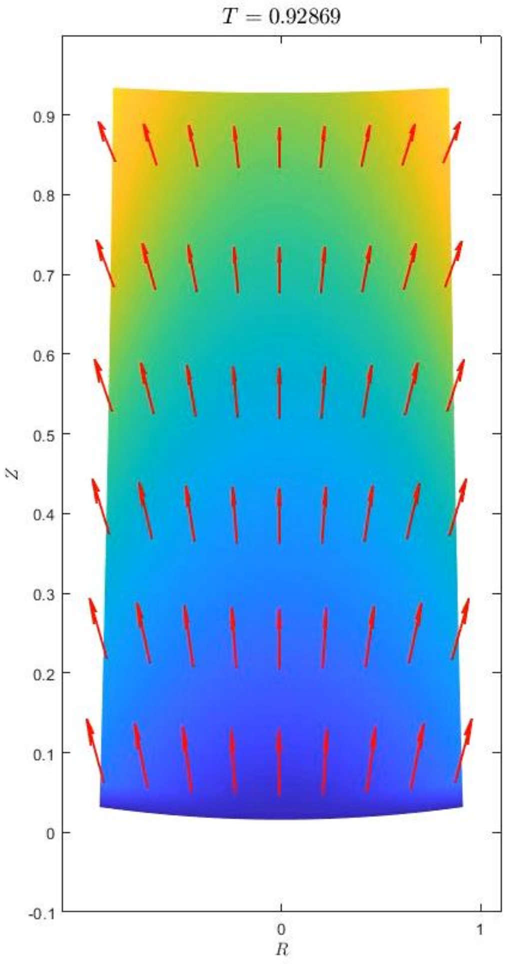
Drying of slender cylinders - comments

- The same approach can be applied when drying from the sides only (and not the top) in order to deduce the displacement field. Note in this case that $\phi = \phi(r,\, z)$ with $\phi = \phi_C(z) + \phi_1(z) r^2$.

- In any case, we approach a steady state when the evaporative flux balances the flux of water drawn up from the base, as illustrated here.

- These results agree with an alternative Lagrangian approach, where the cylinder is comprised of a stack of circular discs, drying isotropically and bending to accommodate differential swelling under classical plate theory.





Conclusions

- Current approaches to modelling super-absorbent hydrogels are either analytically-intractable, and hide the physical processes underlying the swelling and drying, or do not consider the large strains accurately.

- We have introduced a model which linearises around small deviatoric strains but allows for large isotropic strains to treat hydrogels as instantaneously linear-elastic whilst permitting a description of SAPs.

- This model can also describe the displacement field in more complicated multidirectional problems, unlike classical poroelastic approaches, and agrees qualitatively with experiments.

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Webber & Worster *A linear-elastic-nonlinear-swelling theory for hydrogels. Part 1. Modelling of super-absorbent gels*
Webber, Etzold & Worster *A linear-elastic-nonlinear-swelling theory for hydrogels. Part 2. Displacement formulation*
J. Fluid Mech. (in prep)

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