A linear-elastic-nonlinear-swelling model for hydrogels

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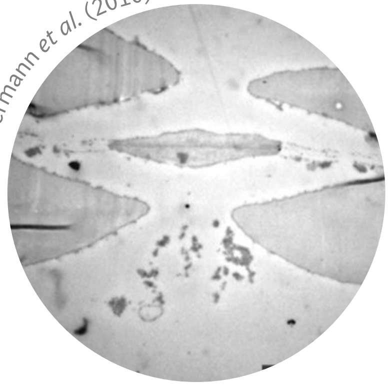
Modelling hydrogels

- Hydrogels are formed of a hydrophilic polymer scaffold surrounded by adsorbed water molecules
  - Can comprise >99% water by volume but remain solid
  - Behave elastically with low shear modulus
  - Can swell or dry to extreme degrees when water is either added or removed

Royal Horticultural Society



Pittermann *et al.* (2010)

Final radius of ~1.5cm

Modelling hydrogels

Fully-nonlinear models

$$W = W_{\mathrm{mix}} + W_{\mathrm{elastic}}$$

- Energy density function with contributions from mixing (entropy, electrostatic interactions, temperature-dependence, …) and elasticity (of individual polymer chains).
- Accurate, models large strains
- Not analytically tractable, parameters hard to determine

Flory & Rehner (1943a,b), Cai & Suo (2012), Bertrand et al. (2016), Butler & Montenegro-Johnson (2022)

Fully-linear models

$$\frac{\partial \phi}{\partial t} = D \frac{\partial^2 \phi}{\partial x^2} \quad \left(D = K + \frac{4}{3}\mu \right)$$

- Based on linear poroelasticity, interstitial flow via Darcy's law. Treats gel as a linear-elastic material.
- Analytically tractable, clear physics, 'macroscopic' parameters
- Can't deal with large swelling strain

Biot (1941), Tanaka & Fillmore (1979), Doi (2009)

Poromechanical modelling

Webber & Worster *and*
Webber, Etzold & Worster
JFM, 2023

Displacement-strain relations

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

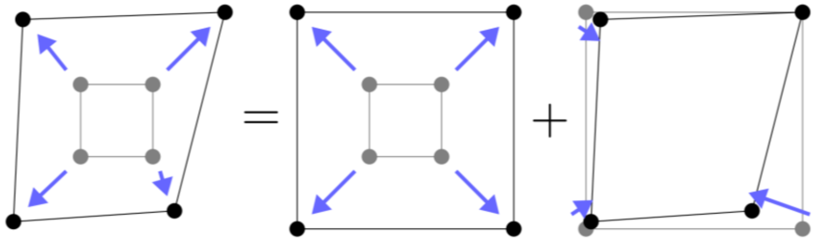
$$\mathbf{e} = \left[1 - \left(\frac{\phi}{\phi_0}\right)^{1/n}\right]\mathbf{I} + \boldsymbol{\epsilon}$$

Deviatoric strain tensor

$$\boldsymbol{\nabla}\cdot\boldsymbol{\xi} = n\left[1 - \left(\frac{\phi}{\phi_0}\right)^{1/n}\right]$$

- **Key idea:** only allow for nonlinearities in isotropic strains corresponding to swelling, and linearise around small deviatoric (~‘shearing’) strains.
- **Alternative statement:** treat a gel *swollen to a given degree* as a linear-elastic material with polymer-fraction-dependent material properties.
- Need a reference state – gel placed in water and allowed to swell uniformly $\phi \equiv \phi_0$

Polymer (volume) fraction



ISOTROPIC **DEVIATORIC**

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$$\boldsymbol{\nabla}\cdot\boldsymbol{\xi} = n\left[1 - \left(\frac{\phi}{\phi_0}\right)^{1/n}\right]$$

Constitutive relation

Shear modulus

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

Effective stress

Osmotic pressure

Pervadic (pore) pressure

- Remain agnostic as to the specific elastic model
- Pressure comes from isotropic elasticity and hydrophilic interactions

Example: Hencky elasticity

$$\boldsymbol{\sigma}^{(e)} = \Lambda(\phi/\phi_0)\,\mathrm{tr}(\mathbf{H})\mathbf{I} + (M - \Lambda)(\phi/\phi_0)\mathbf{H} \qquad \mathbf{H} = \frac{1}{2}\ln\left(\mathbf{F}\mathbf{F}^{\mathrm{T}}\right)$$

$$\Pi(\phi) = \left(\Lambda + \frac{M}{2}\right)\frac{\phi}{\phi_0}\ln\left(\frac{\phi}{\phi_0}\right) \qquad \mu_s(\phi) = \frac{M-\Lambda}{2}\left(\frac{\phi}{\phi_0}\right)^{2/3}$$

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Constitutive relation

Shear modulus
Assume constant

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

Pervadic (pore) pressure

Osmotic pressure
Assume linear, $\Pi = K(\phi - \phi_0)/\phi_0$

Transport equation

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

Advect with total flux

Coefficient from Darcy's law
Permeability over viscosity; assume constant

- Continuity of normal and tangential stress
- Fixed edges
- Continuity of pore pressure

Boundary conditions

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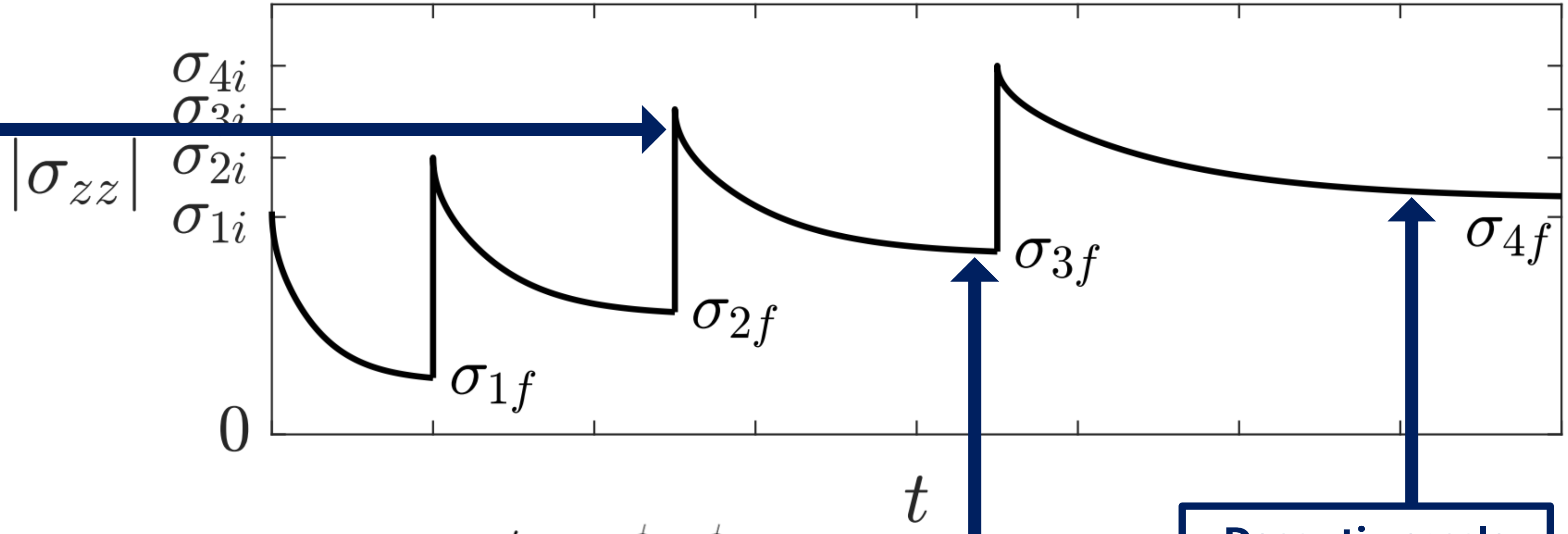
Measuring material properties

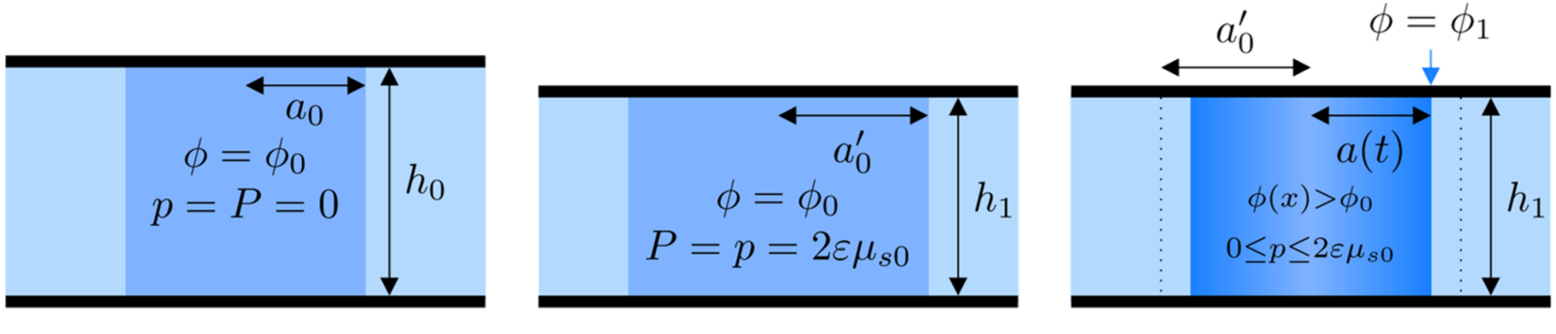
- Only three parameters needed to describe *any* gel, but they depend on degree of swelling.

Initial force (short timescale)
Set by shear modulus
(incompressible deformation)



Decay timescale
Set by permeability

Final force (long timescale)
Set by osmotic pressure
(steady state relaxation)



(a) (b) (c)

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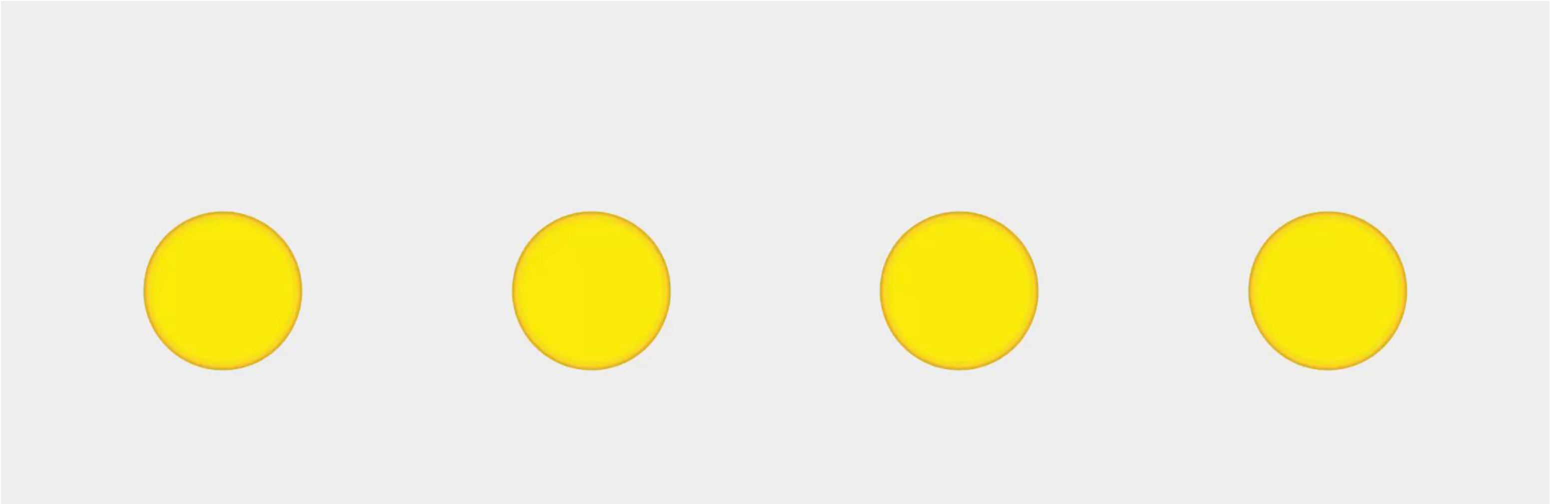
Displacement formulation

- Quasi-one-dimensional problems are easy: shape is set by polymer conservation

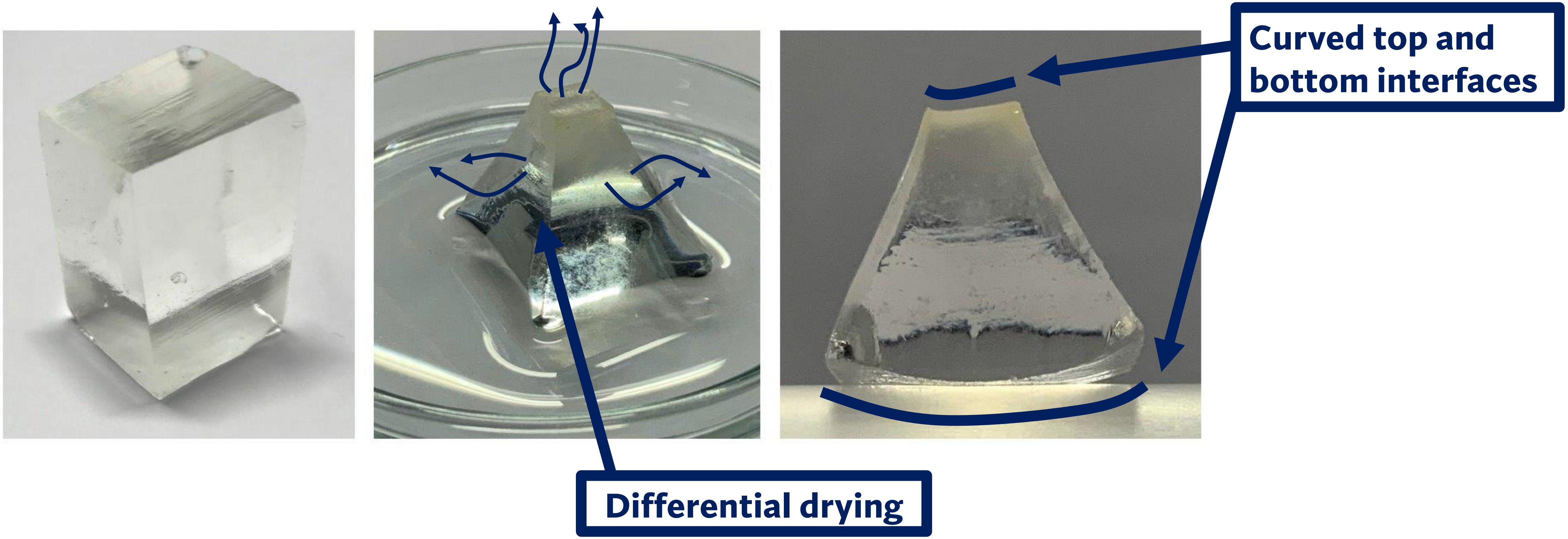


- Need a way to express the shape of a hydrogel as it swells; look to linear elasticity and find a displacement formulation

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

Drying of cylinders

- As an example of the importance of the displacement formulation, model the evaporation of water from the sides of a prism with its base immersed in water.



Experiments and photographs courtesy of Merlin Etzold

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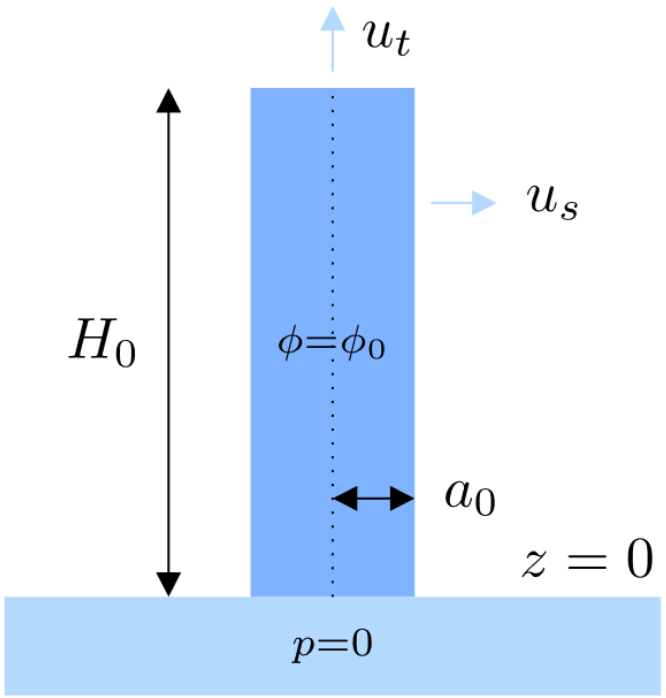

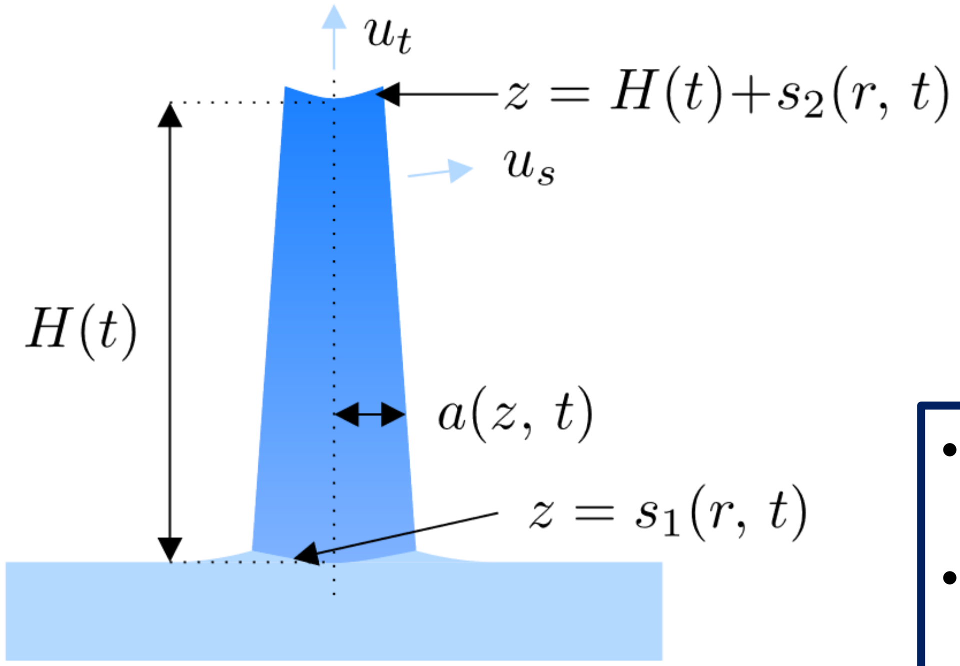

Polymer transport equation

Displacement equation

+

- No normal stress on base
- Evaporative flux conditions on top and sides
- No shear or normal stress on sides

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Drying of cylinders

- Make a slenderness approximation that length is much greater than the radius. This motivates separating the polymer fraction field

$$\phi(r,\, z,\, t) = \phi_C(z,\, t) + \varepsilon^2 \phi_1(r,\, z,\, t)$$

Aspect ratio

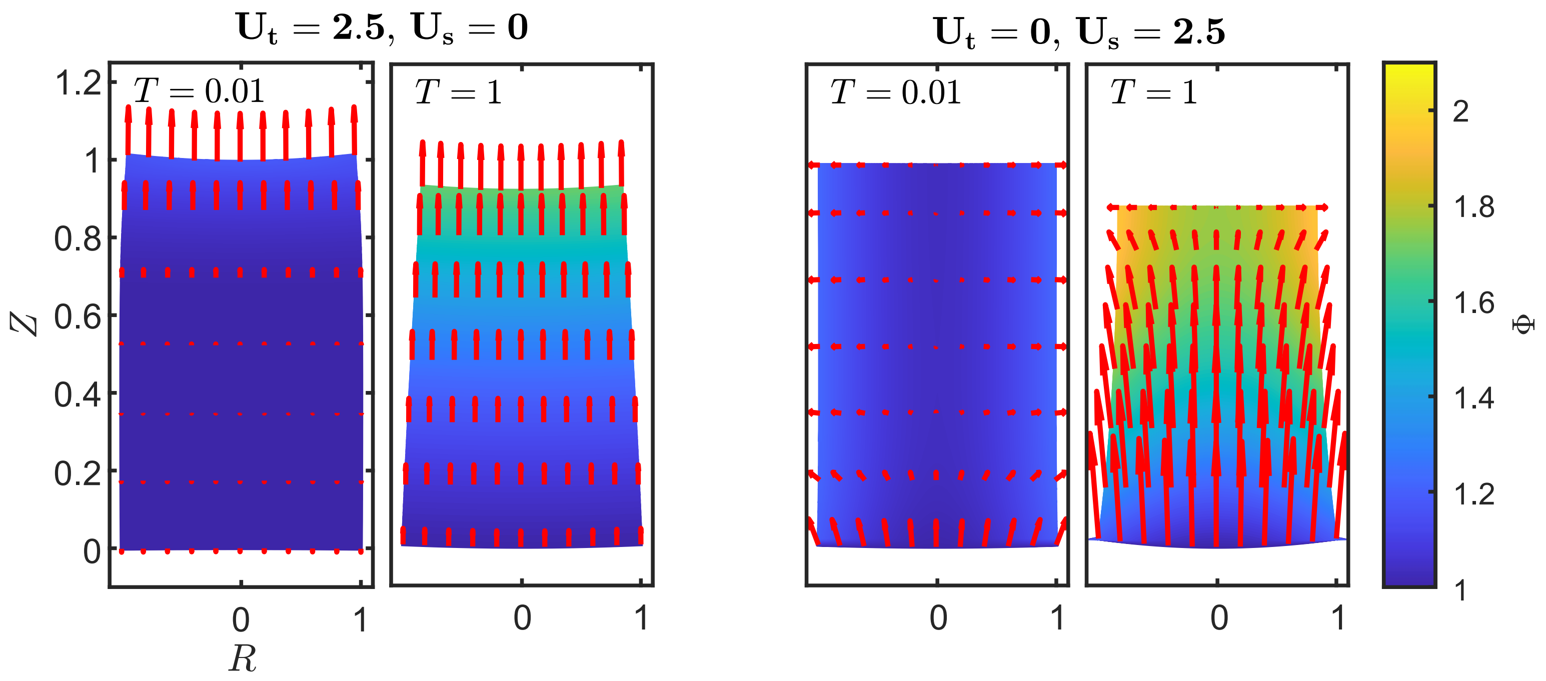
- Separation of variables implies that $\phi_1 \propto r^2$ and thus the small radial variations are set by considering the evaporative flux on the sides, since $u_r \propto \partial\phi/\partial r$

$$\frac{\partial \phi_C}{\partial t} + q_z \frac{\partial \phi_C}{\partial z} = \frac{1}{a^2}\frac{\partial}{\partial z}\left[a^2 D(\phi_C)\frac{\partial \phi_C}{\partial z}\right] + \frac{2\phi_C u_s}{a}$$

$$q_z = \frac{D(\phi_C)}{\phi_C}\frac{\partial \phi_C}{\partial z} - \left(\frac{\phi_C}{\phi_0}\right)^{1/3}\int_0^z \frac{\partial}{\partial t}\left(\frac{\phi_C}{\phi_0}\right)^{1/3} \mathrm{d}z'$$

$$D(\phi_C) = \frac{k}{\mu_l}\left[\frac{K\phi_C}{\phi_0} + \frac{4\mu_s}{3}\left(\frac{\phi_C}{\phi_0}\right)^{1/3}\right]$$

Drying of cylinders

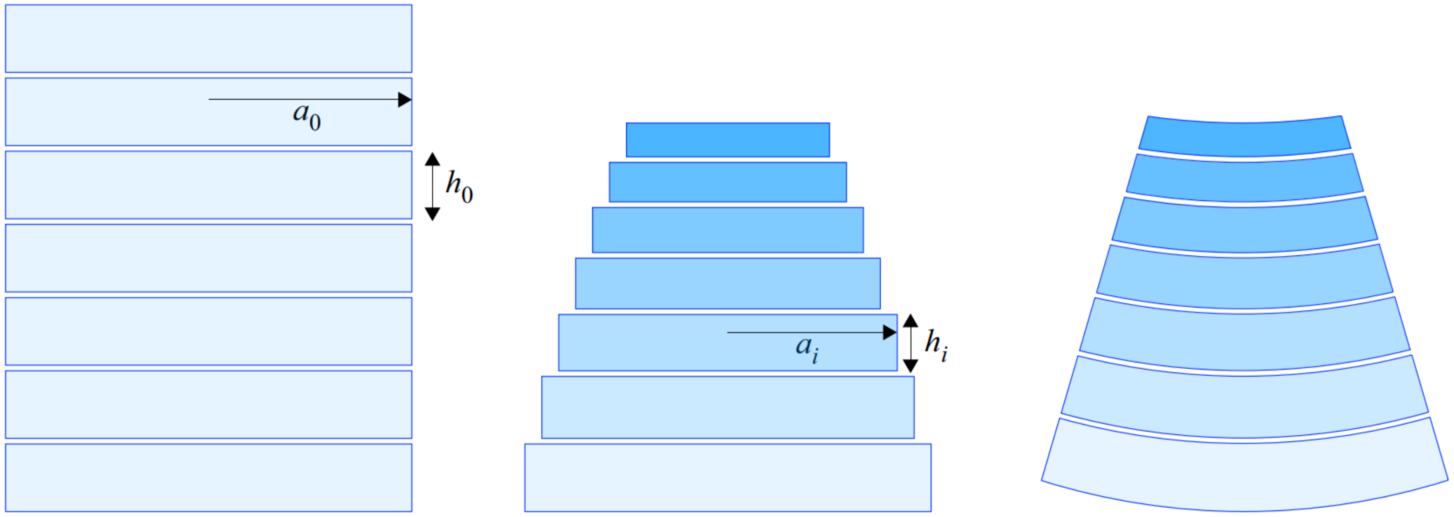


- Expression for radius suggests isotropic contraction at a fixed vertical position
- Height follows from polymer conservation
- Differential drying creates the curved shapes at the top and bottom

$$a(z,\,t) = (\phi_C/\phi_0)^{-1/3} a_0 \qquad h_0 = \int_0^{H(t)} \left[1 - (\phi_C/\phi_0)^{1/3}\right] \mathrm{d}z'$$

$$s_1(r,\,t) = \frac{r^2}{2}\frac{\partial}{\partial z}\left(\frac{\phi_C}{\phi_0}\right)^{1/3}\Bigg|_{z=0} \qquad s_1(r,\,t) = \frac{r^2}{2}\frac{\partial}{\partial z}\left(\frac{\phi_C}{\phi_0}\right)^{1/3}\Bigg|_{z=H(t)}$$

Drying of cylinders



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Wrinkling instabilities

Webber & Worster
Phys Rev E, 2024

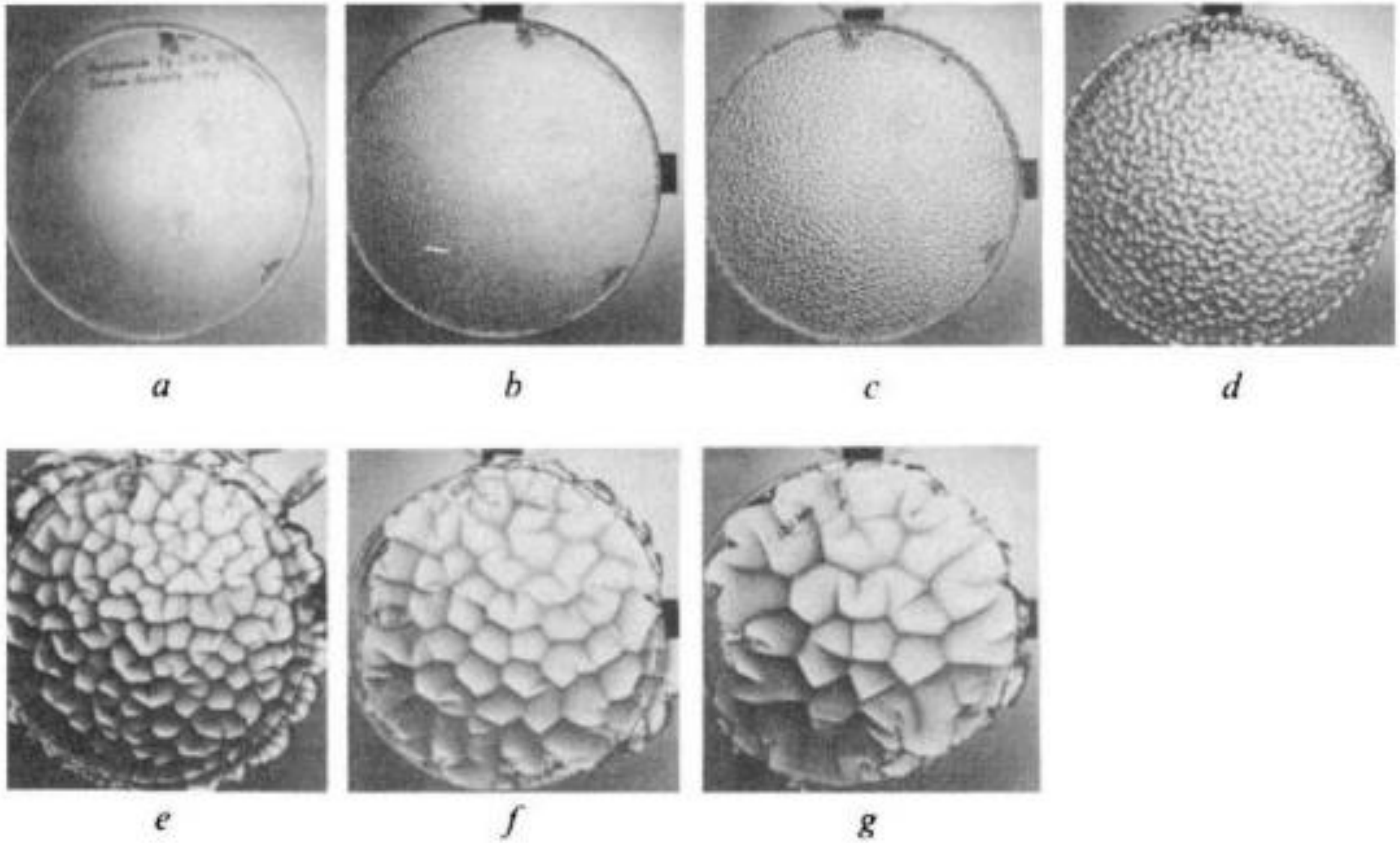

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Figure from Tanaka *et al.*, Nature **325:**796-798, 1987

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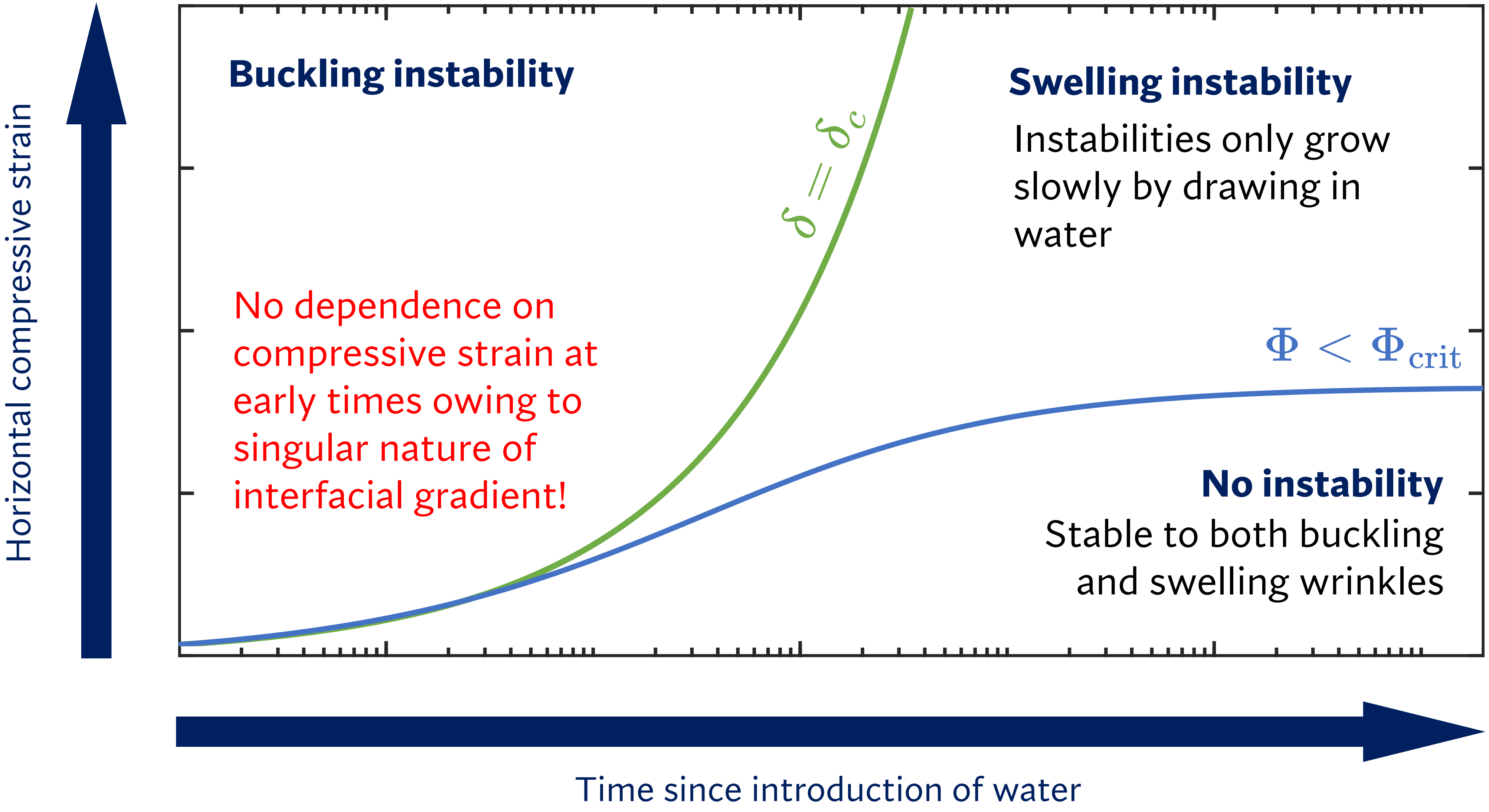

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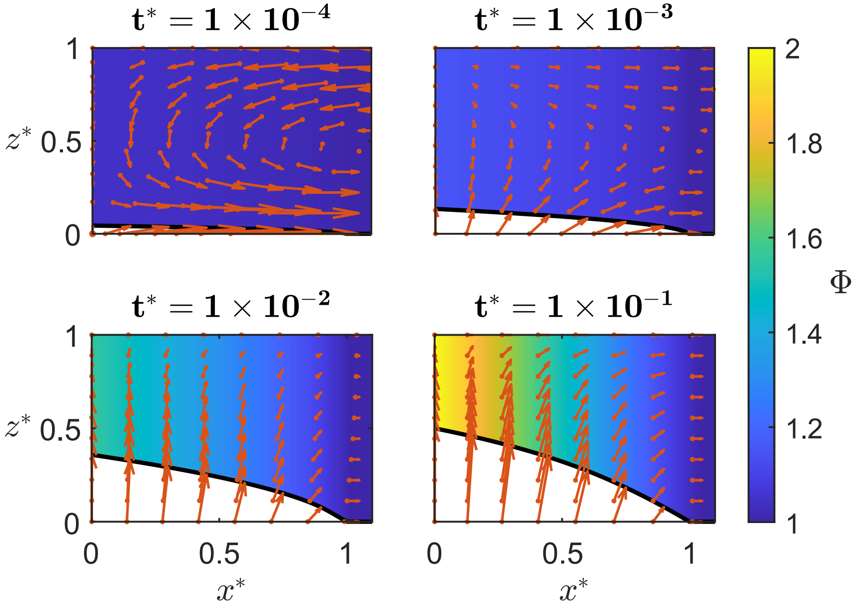
Freezing damage

SPECULATIVE EARLY WORK

- If brought to relatively cool temperatures, water will not freeze in place in gel pores – it will instead segregate, forming an ice layer and dried gel.

- Can we model the so-called 'cryosuction' process where water is drawn from a gel to form ice – this will provide a good analogue for freezing damage in brittle porous media?

- Maybe:



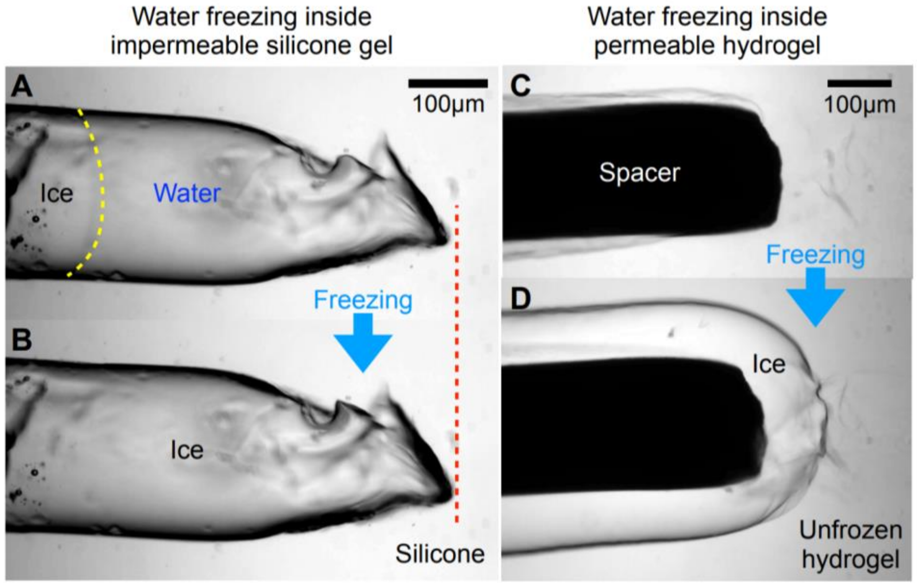


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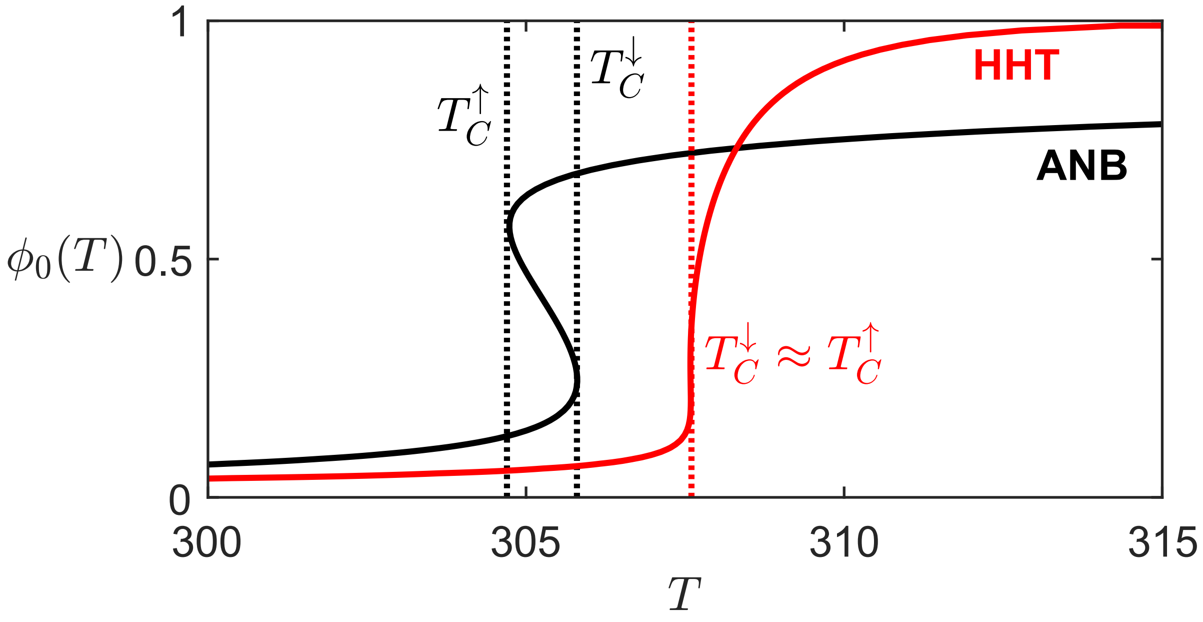
Figure from Yang *et al.*, arXiv **2401.**12871, 2024

Thermo-responsive gels

SPECULATIVE EARLY WORK

- A huge number of practical behaviours depend on gels whose properties change significantly with changes in temperature.



- This can be explained in LENS using an equilibrium polymer fraction (and thus osmotic pressure) that depends on temperature

$$\Pi(\phi, T) = \tilde{\Pi}\left\{\Omega^{-1}\left(\phi - \phi^{1/3}\right) + \phi^2(1-\phi)\left(A_1 + B_1 T\right) - \log\left(1-\phi\right) - \phi - \phi^2\left[A_0 + B_0 T + (A_1 + B_1 T)\phi\right]\right\}$$

$$\phi_0 \approx \phi_0^{(0)} + \frac{\phi_0^{(\infty)} - \phi_0^{(0)}}{2}\left[1 + \tanh\frac{T - T_C}{\Delta T}\right]$$

Conclusions

- Can model large-swelling gels by allowing isotropic strains to be big, but linearise around deviatoric strains
- This gives a *continuum-mechanical, tractable* model with swelling driven by *interstitial fluid flow* and response governed by *measurable material parameters*
- Can accurately capture large-swelling behaviour with no recourse to micro-scale physics
- Easy to apply to a wide range of problems and post-hoc justification of our assumptions can be sought
- Also possible to add in new physics (freezing, thermo-responsive gels) to model complicated behaviour

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Webber, J. J. & Worster, M. G. *A linear-elastic-nonlinear-swelling theory for hydrogels. Part 1. Modelling of super-absorbent gels*
J. Fluid Mech. **960**:A37 (2023)

Webber, J. J., Etzold, M. A. & Worster, M. G. *A linear-elastic-nonlinear-swelling theory for hydrogels. Part 2. Displacement formulation*
J. Fluid Mech. **960**:A38 (2023)

Webber, J. J. & Worster, M. G. *Wrinkling instabilities of swelling hydrogels*
Phys. Rev E **109**:044602 (2024)

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