A linear-elastic-nonlinear-swelling model for hydrogels

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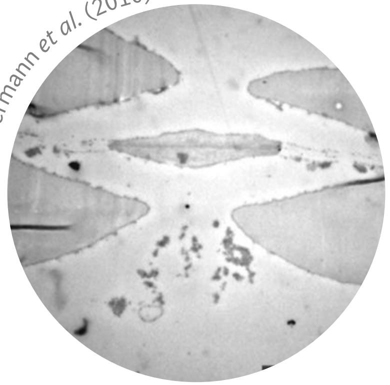
Modelling hydrogels

- 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)



Time immersed in water (~hours)

Final radius of ~1.5cm

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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

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

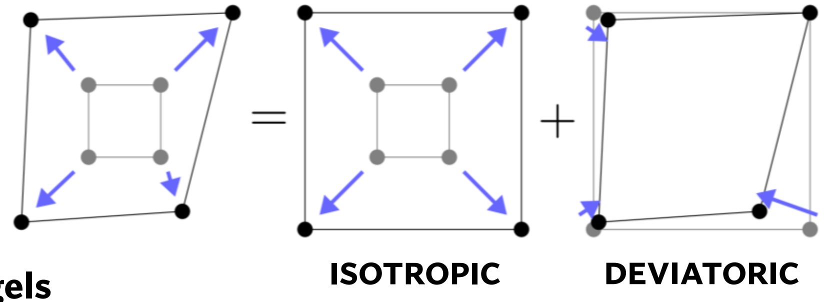
$$\mathbf{e} = \left[1 - \left(\frac{\phi}{\phi_0}\right)^{1/n}\right]\mathbf{I} + \boldsymbol{\epsilon}$$

Deviatoric strain tensor

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

- **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



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Deviatoric strain tensor

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

- Want to relate stresses to strains, with

$$\boldsymbol{\sigma} = -P\,\mathbf{I} + \boldsymbol{\sigma}_{\mathrm{dev}}$$

$P = \Pi(\phi) + p$

depends only on deviatoric strain

- Assume linearity and local isotropy in deviatoric response, so

$$\boldsymbol{\sigma}_{\mathrm{dev}} = \mathbf{C} : \boldsymbol{\epsilon} = 2\mu_s(\phi)\,\boldsymbol{\epsilon}$$

- Flows are driven through the gel *via* gradients in pervadic pressure

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

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Deviatoric strain tensor

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

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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Deviatoric strain tensor (↑ $\boldsymbol{\epsilon}$)

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

Constitutive relation

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

Shear modulus

Effective stress

Osmotic pressure

Pervadic (pore) pressure

- Take each phase to be individually incompressible

$$\frac{\partial\phi}{\partial t} + \boldsymbol{\nabla}\cdot(\phi\boldsymbol{u_p}) = 0 \qquad \frac{\partial}{\partial t}(1-\phi) + \boldsymbol{\nabla}\cdot\left[(1-\phi)\boldsymbol{u_l}\right] = 0$$

and define

$$\boldsymbol{u} = (1-\phi)\left(\boldsymbol{u_l} - \boldsymbol{u_p}\right) \qquad \boldsymbol{q} = \boldsymbol{u} + \boldsymbol{u_p}$$

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

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Deviatoric strain tensor

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

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

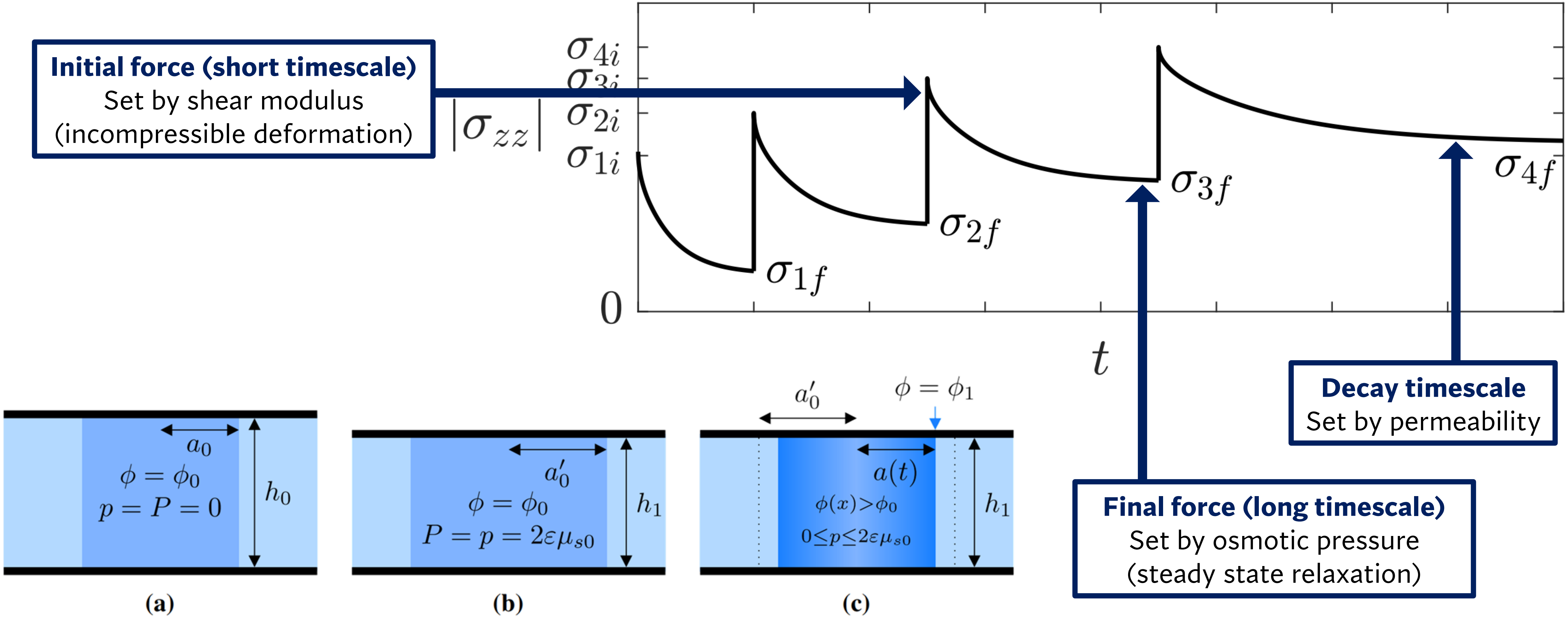
Coefficient from Darcy's law
Permeability over viscosity; assume constant

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

Boundary conditions

Measuring material properties

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



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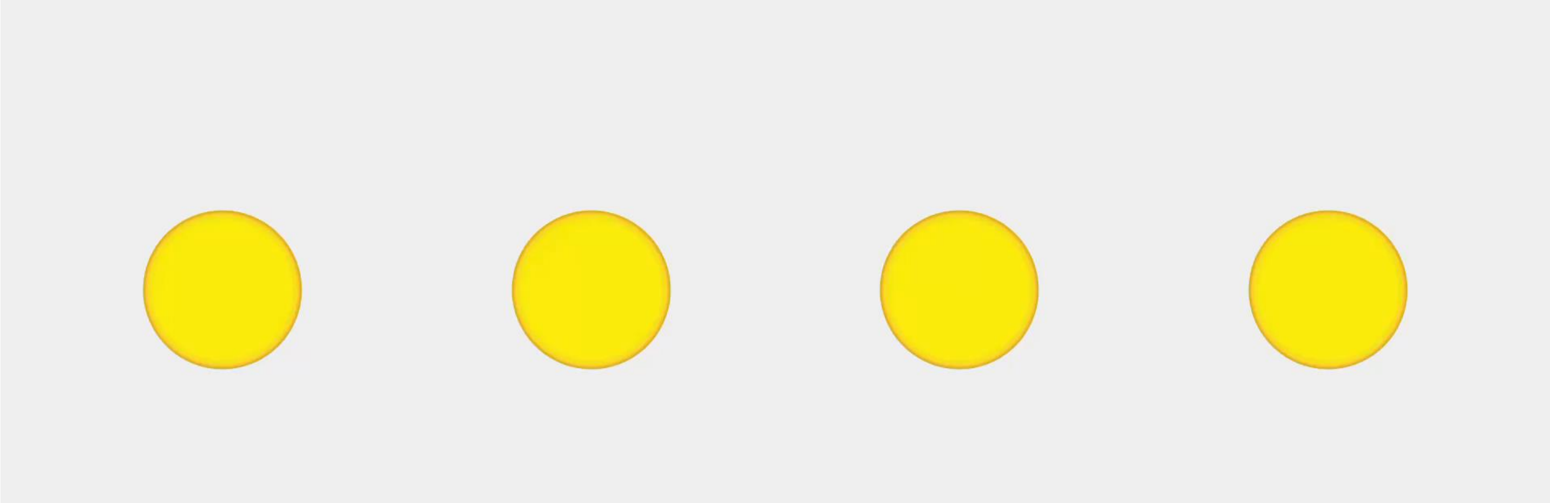
Displacement formulation

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



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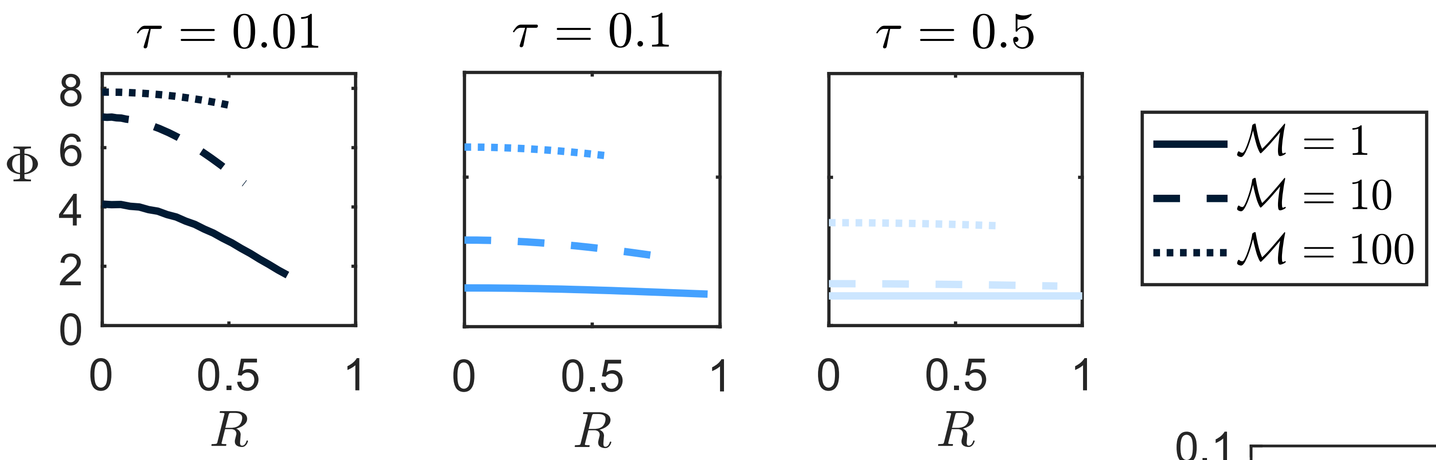

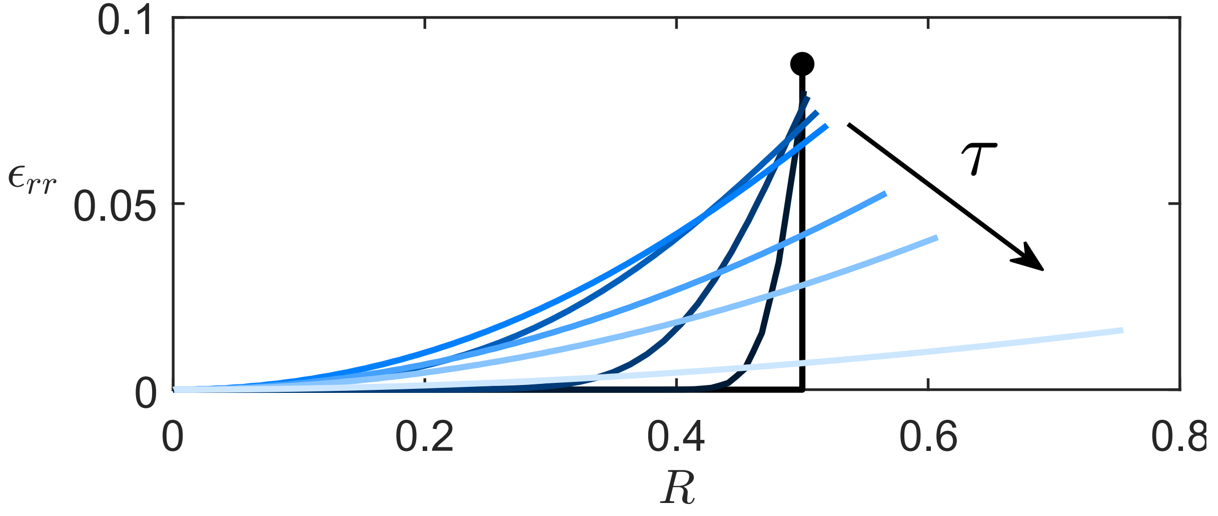

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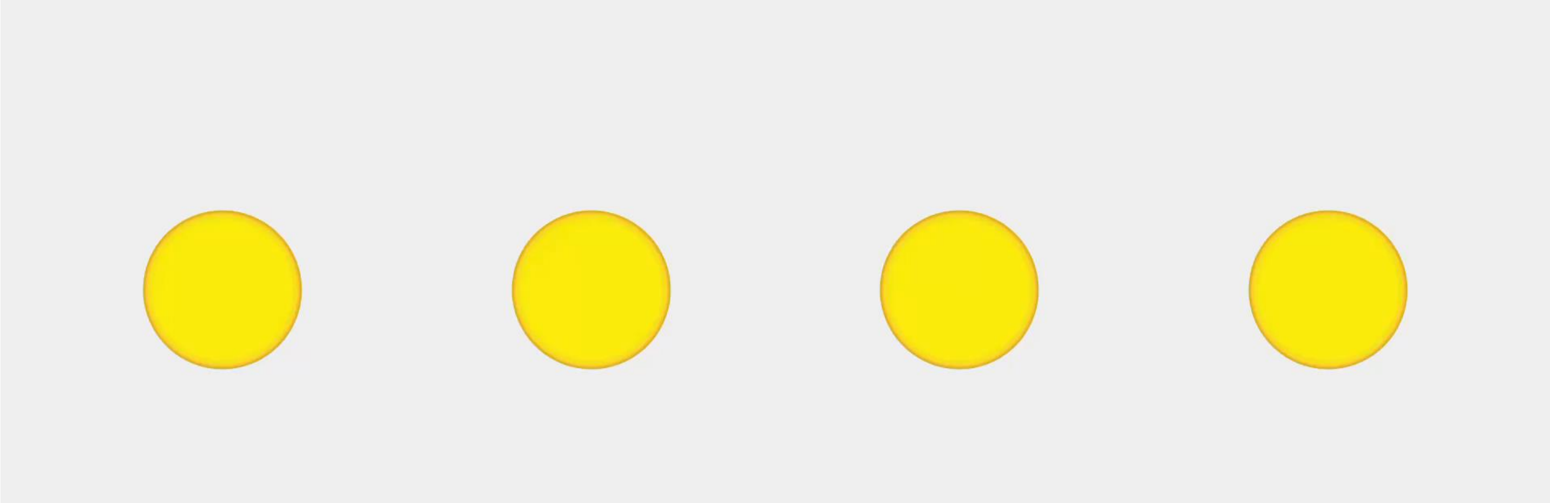
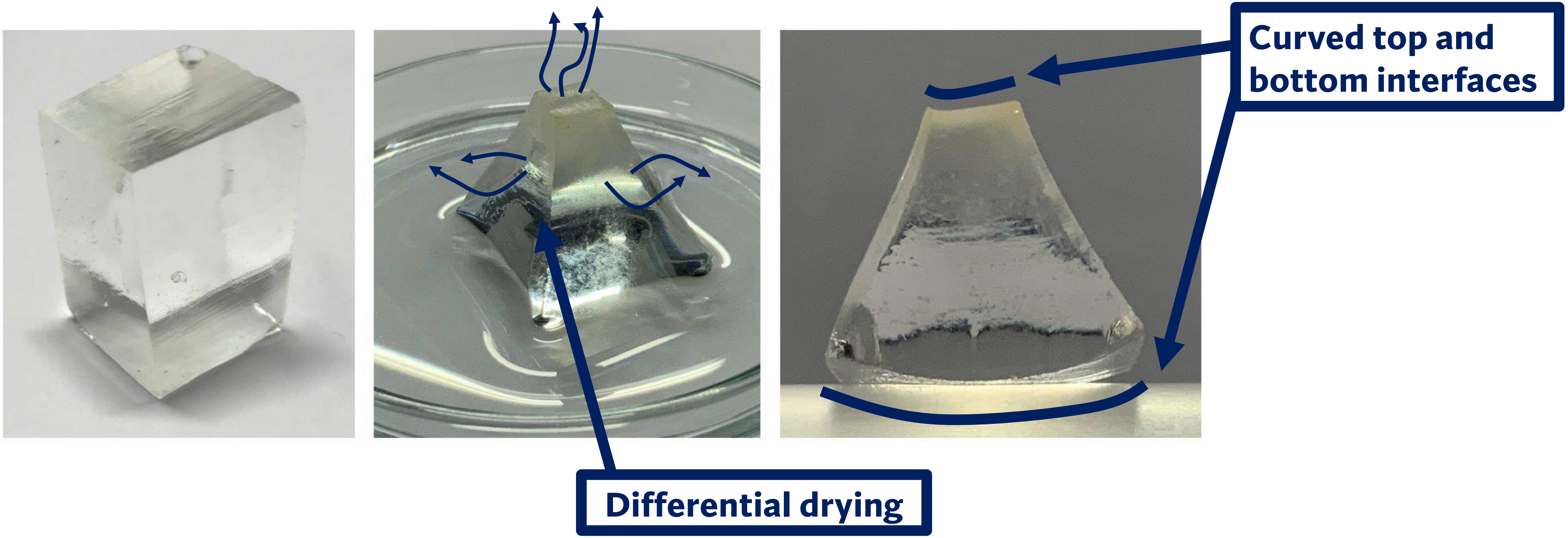


- Need a way to express the shape of a hydrogel as it swells; look to linear elasticity and find a displacement formulation

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

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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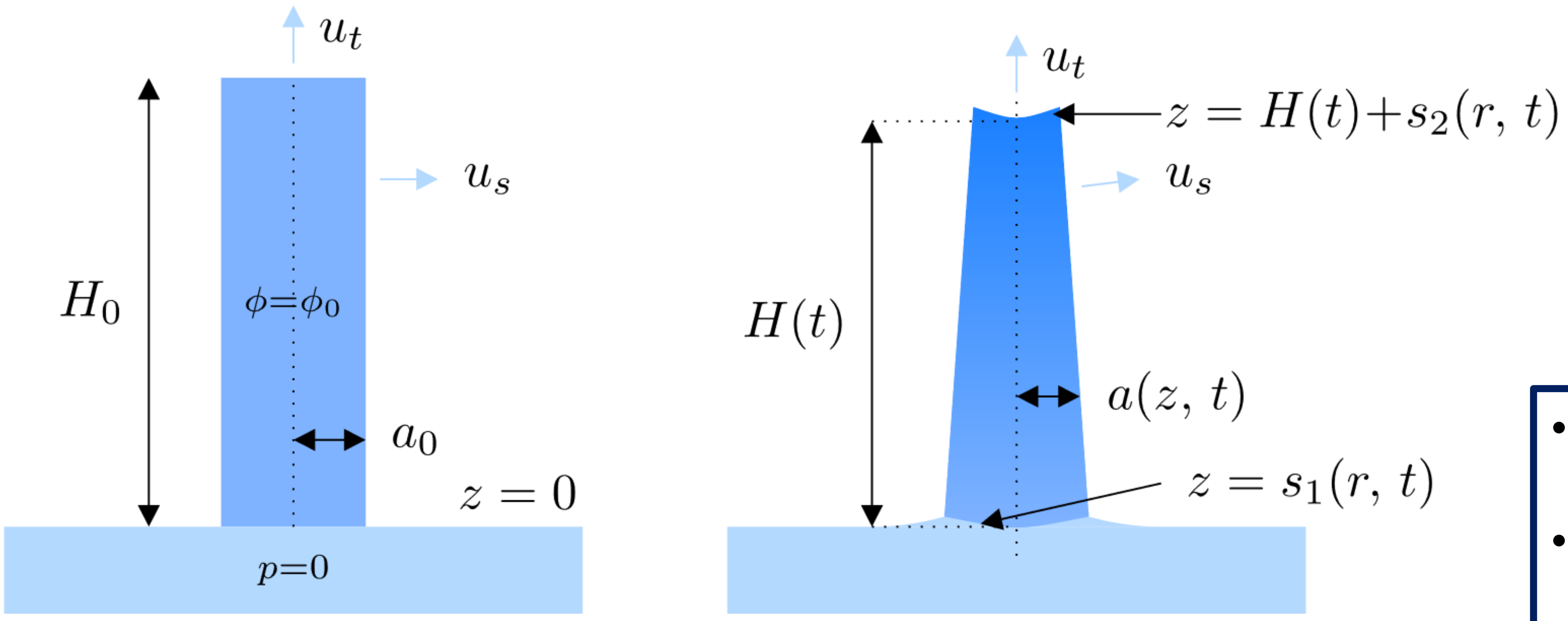

Polymer transport equation

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 $u_r \propto \partial\phi/\partial r$

$$u_t = \frac{D(\phi_C)}{\phi_C}\frac{\partial \phi_C}{\partial z}\bigg|_{\text{top}}$$

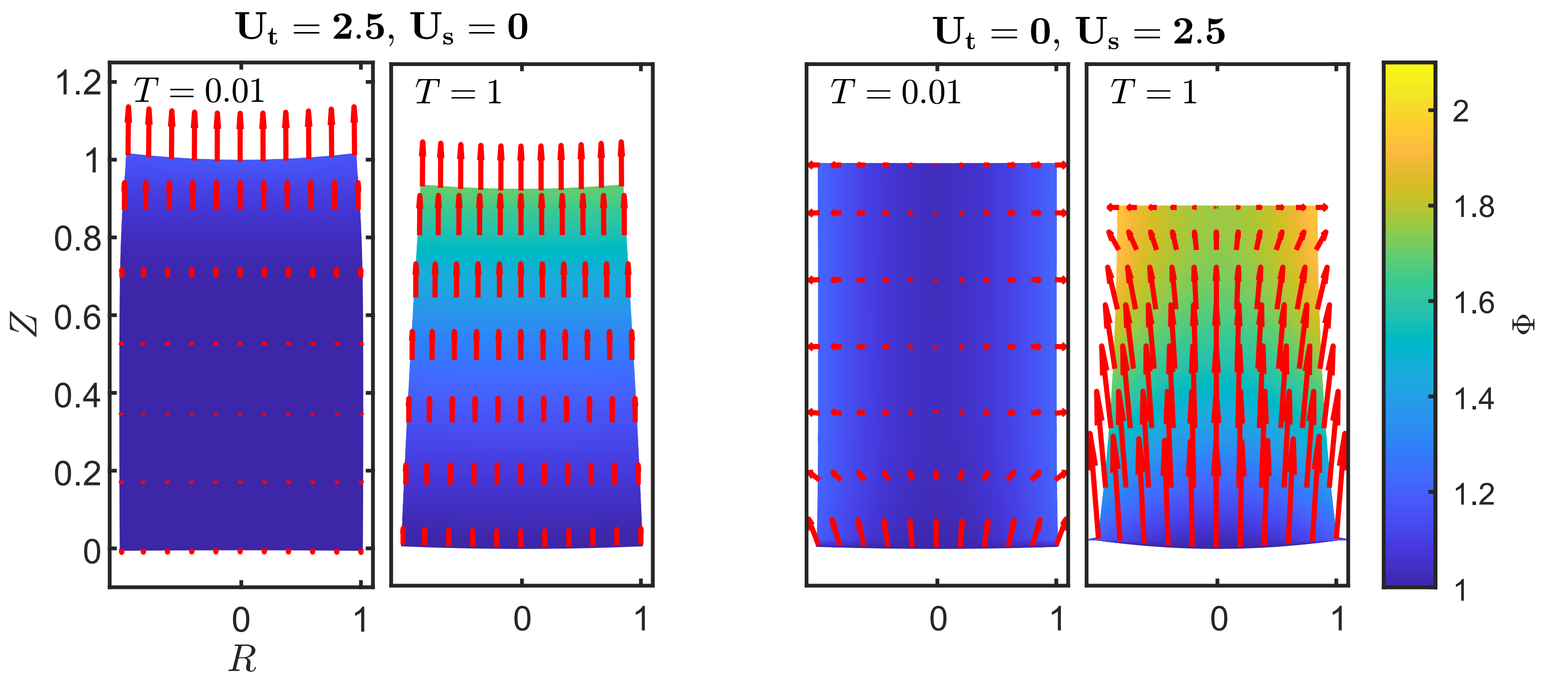
$$\frac{\partial \phi_C}{\partial t} + q_z \frac{\partial \phi_C}{\partial z} = \frac{1}{a^2}\frac{\partial}{\partial z}\left[a^2 D(\phi_C)\frac{\partial \phi_C}{\partial z}\right] + \frac{2\phi_C u_s}{a}$$

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

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

$$u_s = u - v\frac{\partial a}{\partial z} = \frac{D(\phi_C)}{\phi_C}\left[\varepsilon^2\frac{\partial \phi_1}{\partial r} - \frac{\partial \phi_C}{\partial z}\frac{\partial a}{\partial z}\right]$$

Drying of cylinders

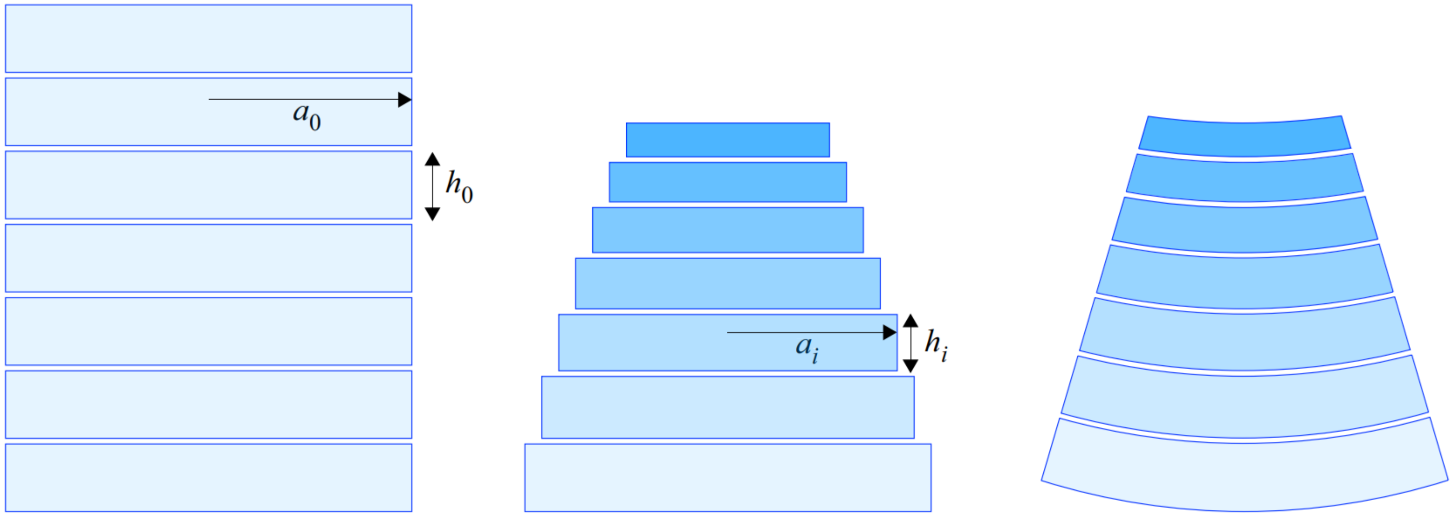


$$a(z,\, t) = (\phi_C/\phi_0)^{-1/3} a_0 \qquad h_0 = \int_0^{H(t)} \left[1 - (\phi_C/\phi_0)^{1/3}\right] \mathrm{d}z'$$

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

- 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

Drying of cylinders



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Wrinkling instabilities

Webber & Worster
Phys Rev E, 2024

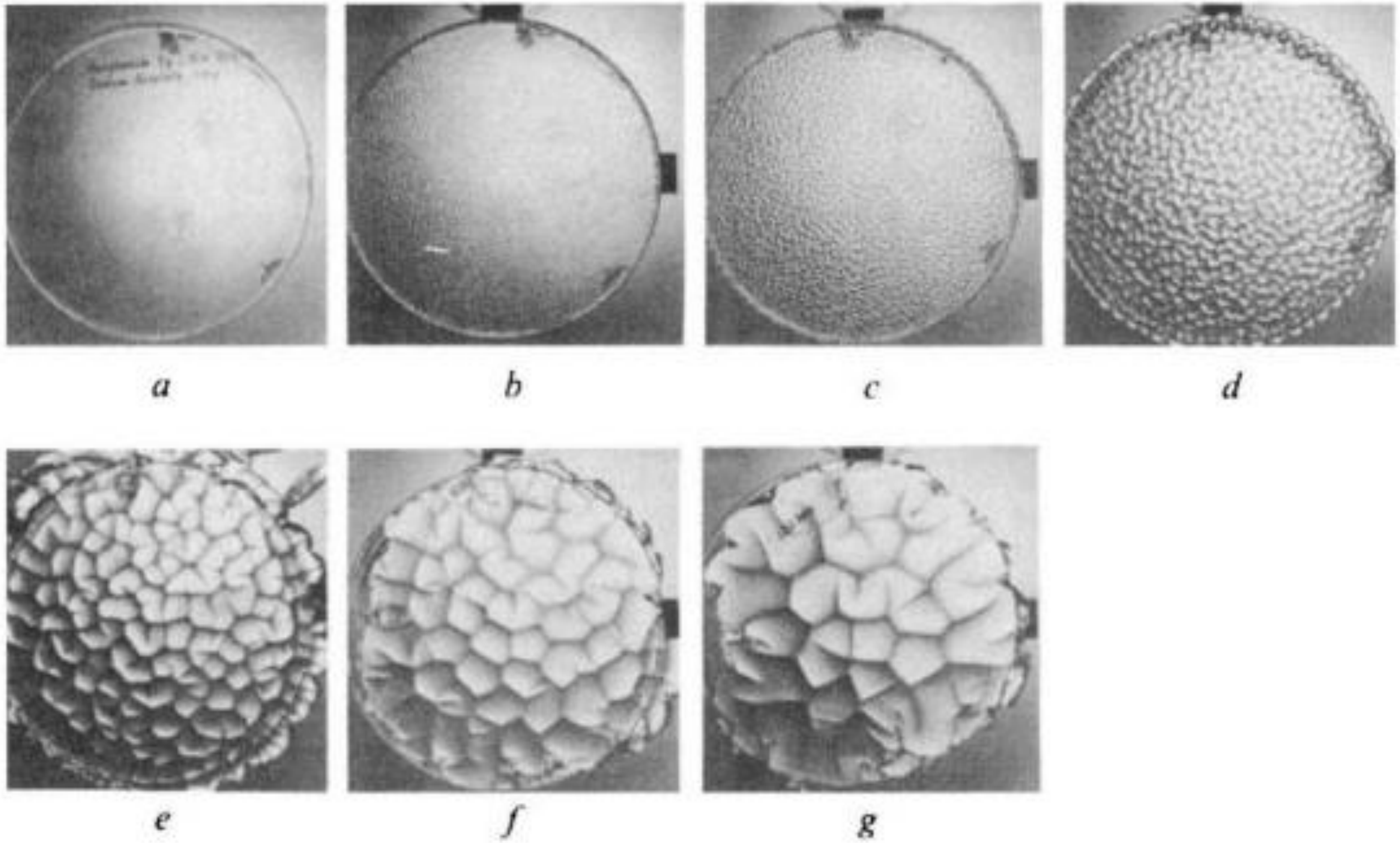

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Figure from Tanaka *et al.*, Nature **325:**796-798, 1987

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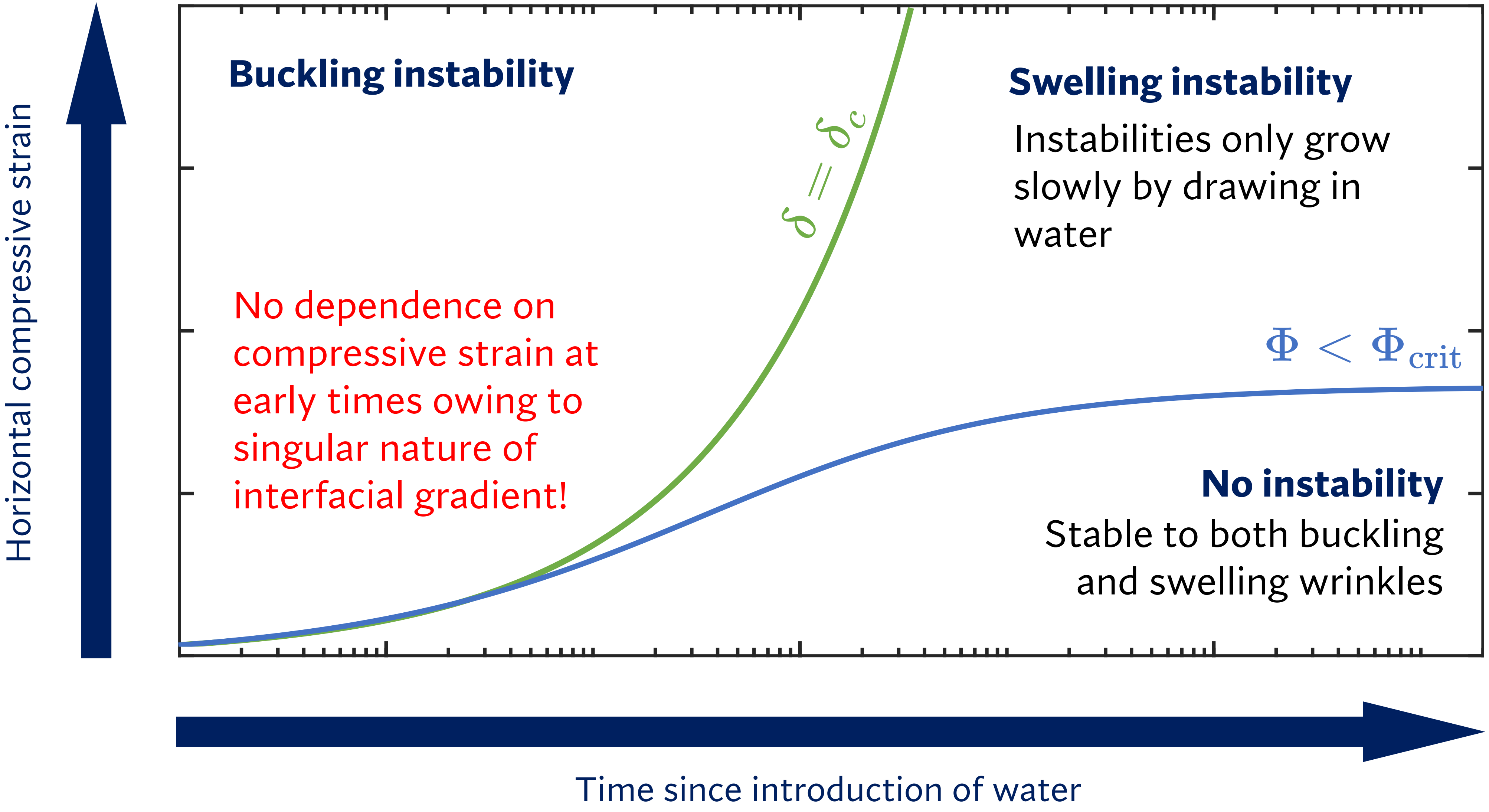

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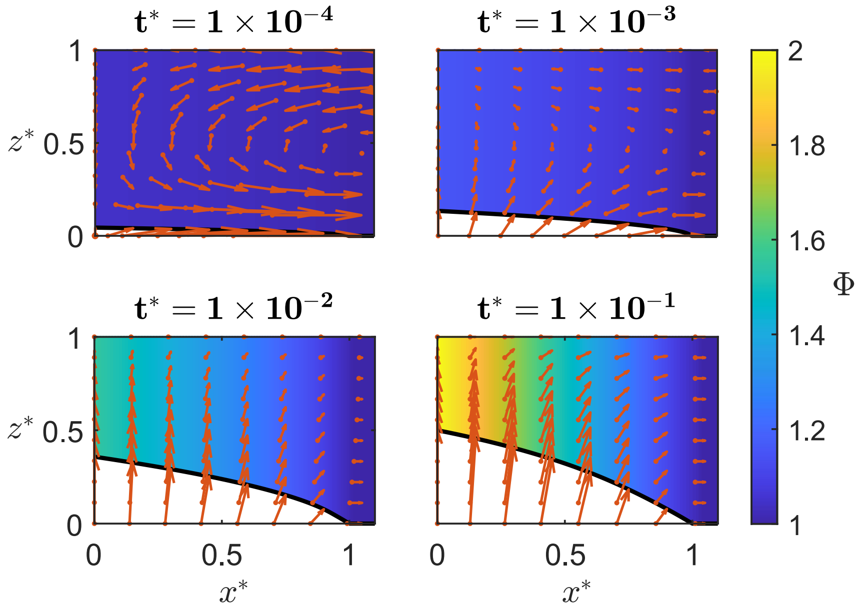
Freezing damage

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:



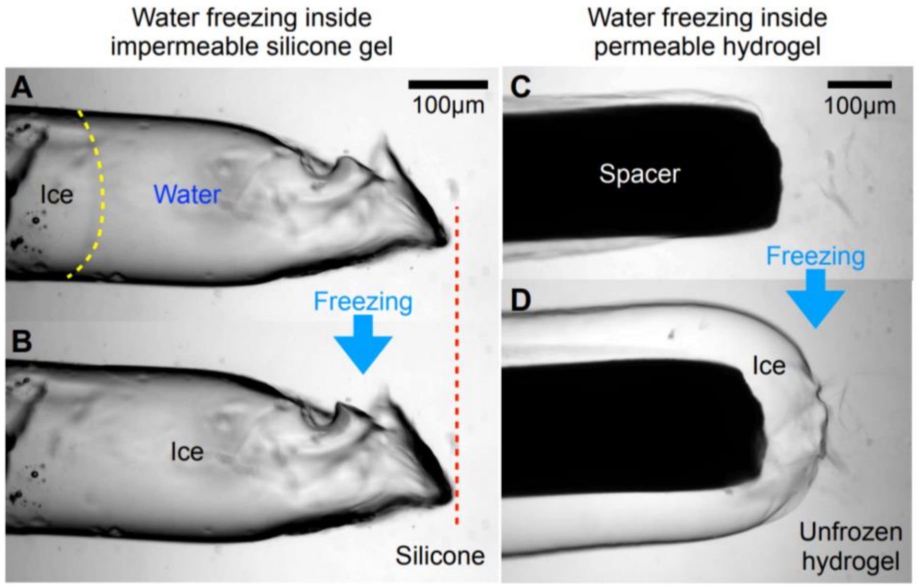


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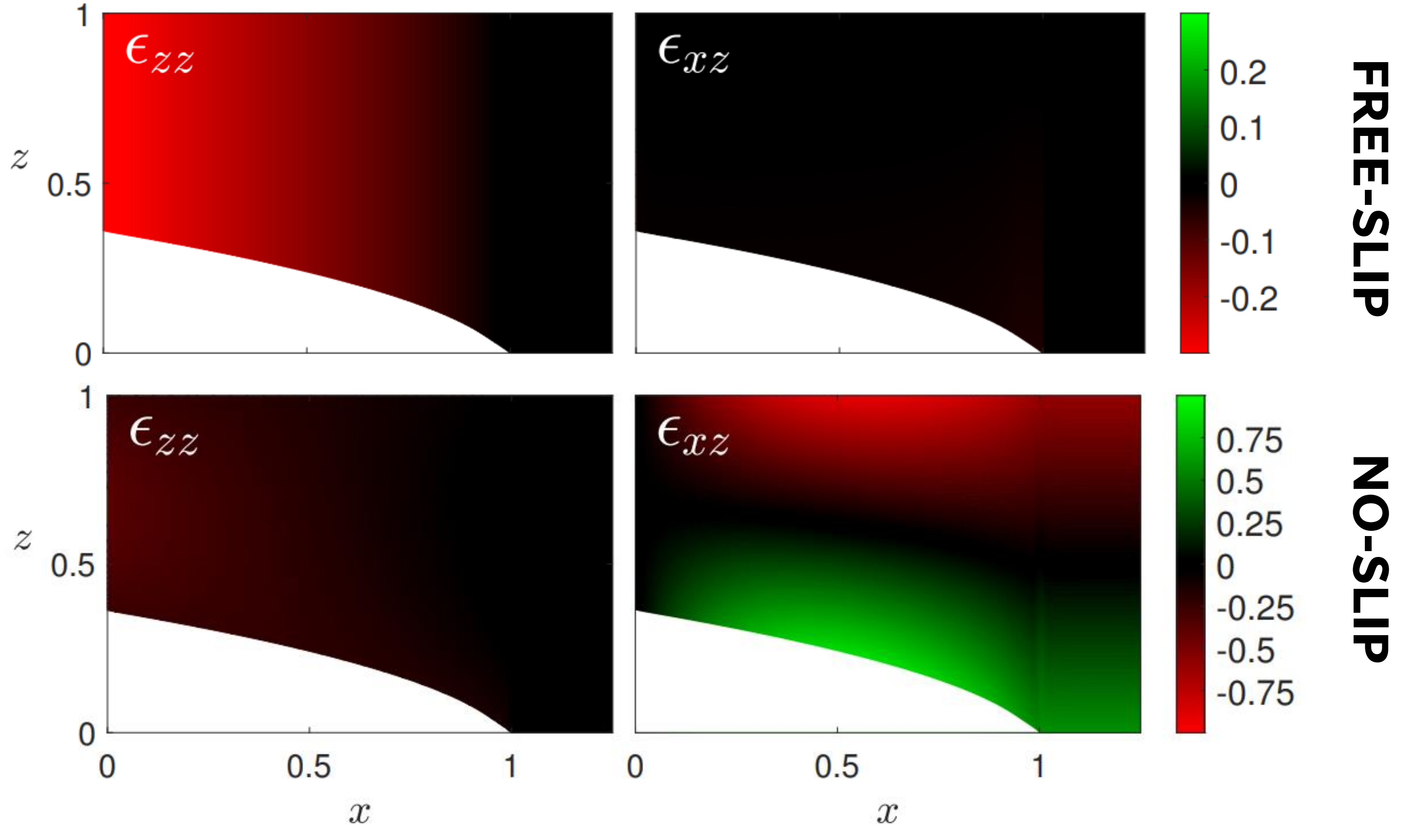
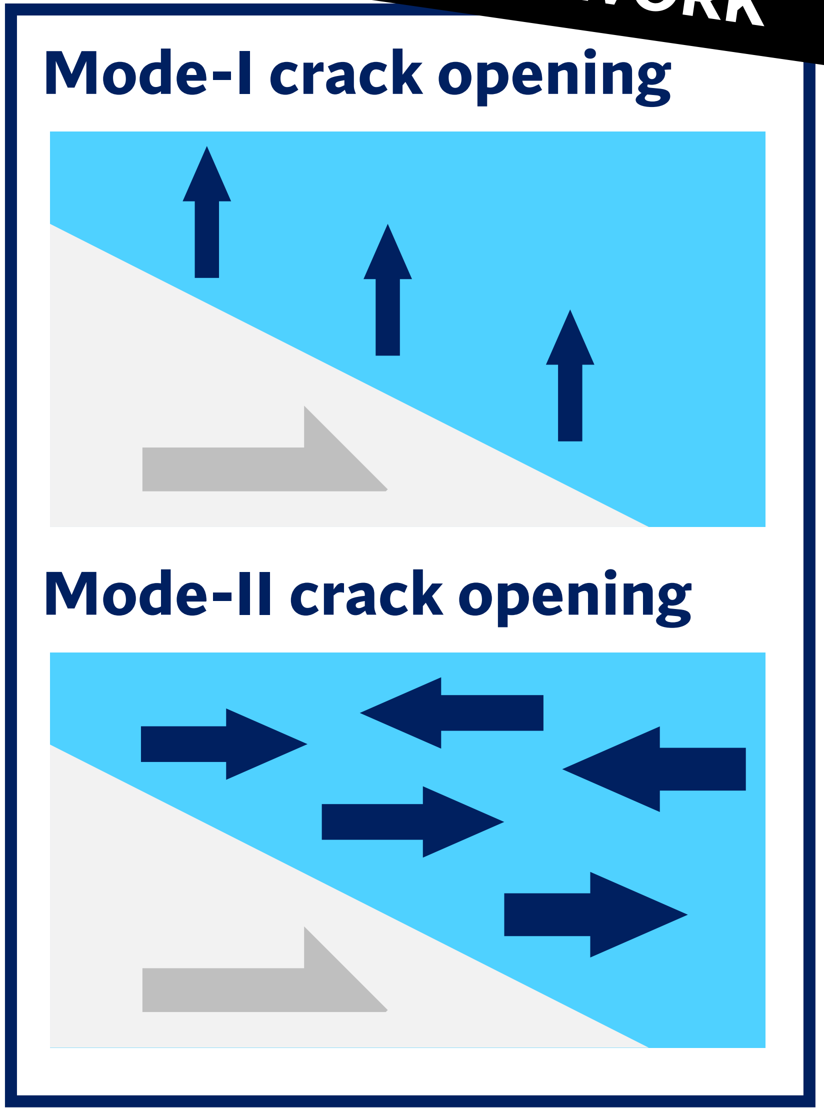
Figure from Yang *et al.*, arXiv **2401.**12871, 2024

Freezing damage

- This shows that the crack opening depends heavily on boundary conditions





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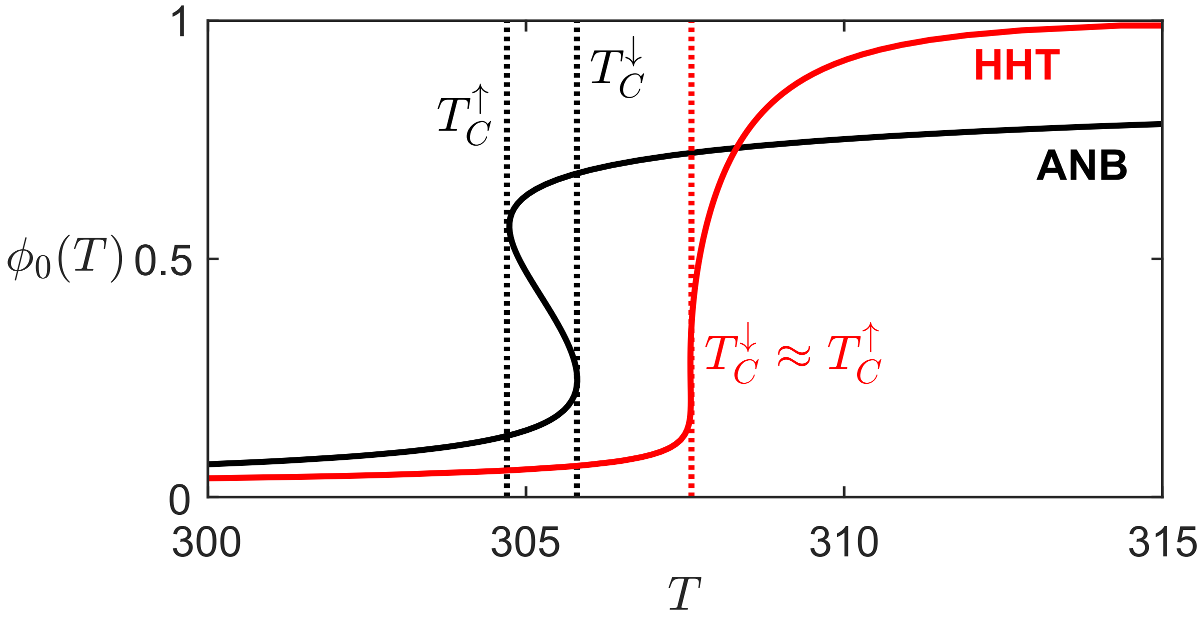
Thermo-responsive gels

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

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

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

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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