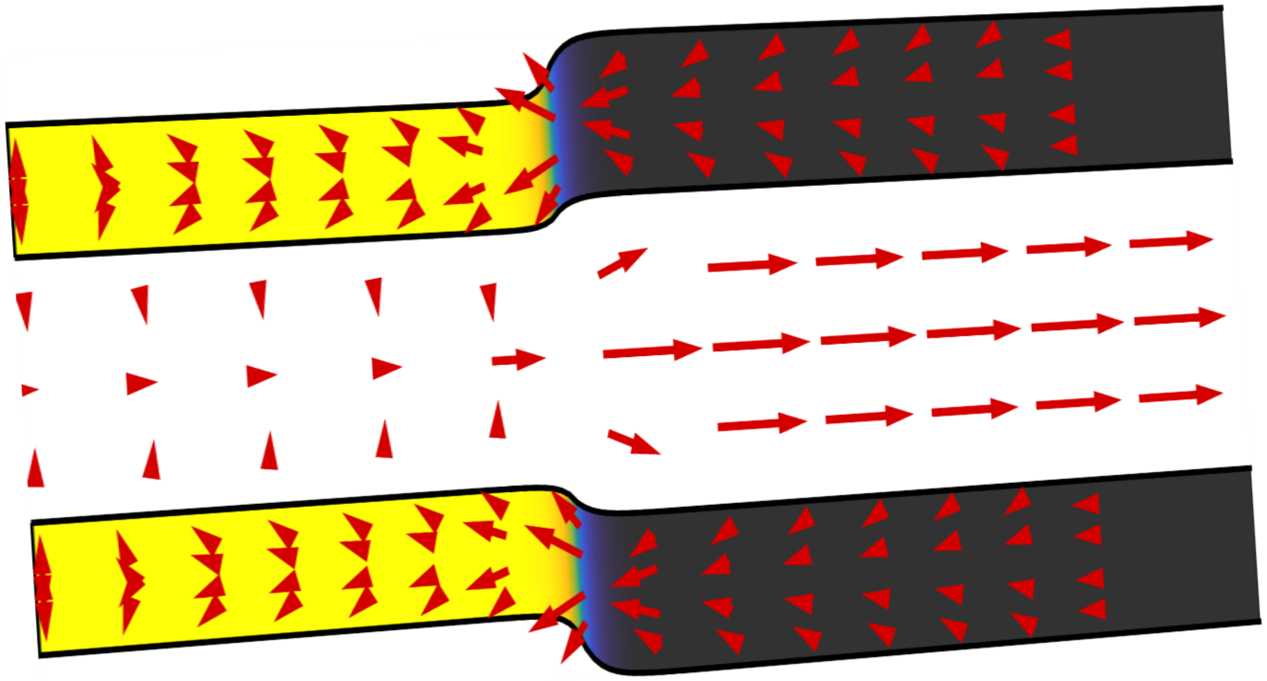

Modelling hydrogels at both ends of the temperature spectrum

Joseph Webber, University of Warwick

with Grae Worster (University of Cambridge) and Tom Montenegro-Johnson (University of Warwick)

ETH Zurich Department of Materials, 27th May 2025

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Overview

1. Thinking about gels like a mathematician

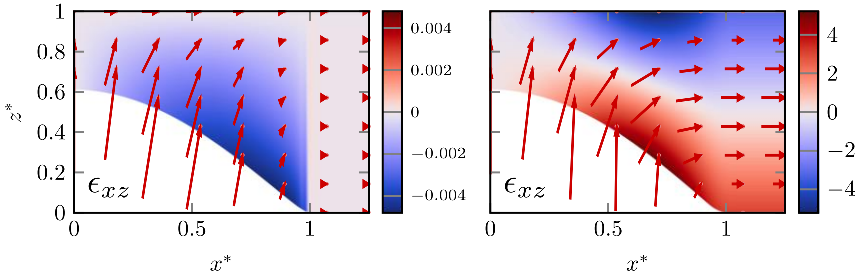
Osmosis · elastic stresses · equilibrium swelling · transport of water · shape change in swelling/drying · behaviour at interfaces · characterising a gel

Temperature (representative values)

270 K — 300 K — 310 K

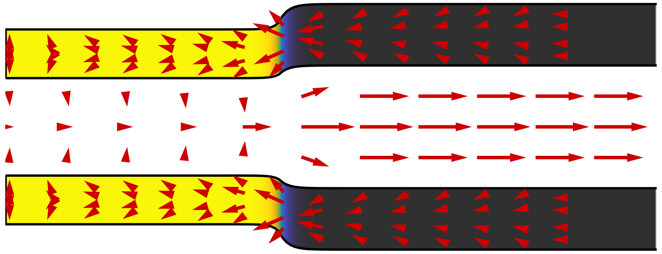
2. Freezing hydrogels at low*(-ish)* temperatures

Formation of pure ice · cryosuction · applying our model to GelFrO · a 2D model · stress buildup



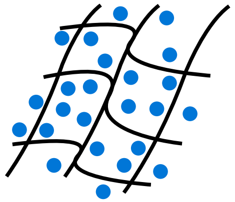
3. Building with thermo-responsive gels

Heating effects on swelling · heat transfer in gels · building pumps with collapsing tubes



What, another gel model?

Usual approach: an energy density function with contributions from everything that could affect behaviour.



polymer volume fraction

$$\mathcal{W} = \underbrace{\frac{k_B T}{2\Omega_p}\left[\mathrm{tr}\left(\mathbf{F_d}\,\mathbf{F_d^T}\right) - 3 + 2\log\phi\right]}_{\text{Gaussian-chain elasticity}} + \underbrace{\frac{k_B T}{\Omega_f}\left[\frac{1-\phi}{\phi}\log(1-\phi) + \chi(\phi, T)(1-\phi)\right]}_{\text{Mixing of polymer and water}}$$

Gaussian-chain elasticity

Mixing of polymer and water

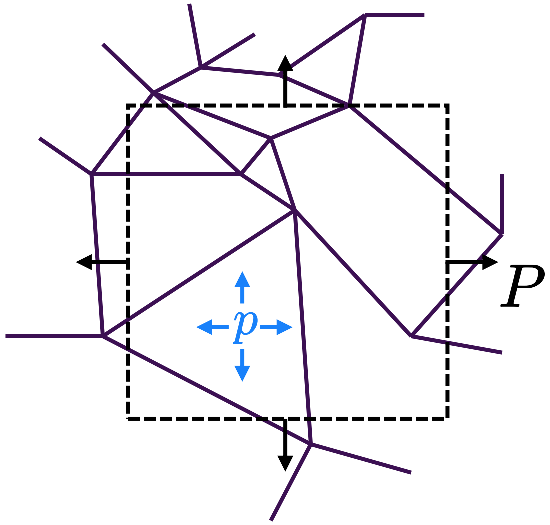
- Messy and very specific for certain gels – lots of parameters
- Not ‘macroscopic’ enough in nature – elasticity ignores water
- Measured relative to a dry state: is this ever physically realisable?
- Transient states are harder to describe than equilibria

Flory & Rehner (1943) *J. Chem. Phys.* ***11***:*512-520*; Flory & Rehner (1943) *J. Chem. Phys* ***11:***521-526; Cai & Suo (2011) *Europhys. Lett.* ***97:***34009

What, another gel model?

A geophysicist's approach: separate contributions from stress into a 'pore pressure' and an 'effective stress'

$$\boldsymbol{\sigma} = -p\mathbf{I} + \boldsymbol{\sigma}_{\text{eff}}$$



Bulk pressure (or thermodynamic pressure) the isotropic stress exerted by a sample of gel; our familiar concept of pressure

Pervadic pressure (or Darcy pressure, "pore" pressure) is the pressure as would be measured by a transducer separated by a partially-permeable membrane from the gel.

$$P = p + \Pi$$

osmotic effects?
isotropic elasticity?
generalised osmotic pressure

In soil science: p is the pore pressure, P is the overburden pressure
In colloids: p is [related to] the chemical potential, Π is the osmotic pressure

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

permeability
relative fluid flux
(dynamic) viscosity of fluid

Biot (1941) *J. Appl. Phys.* ***12:****155-164*; Peppin *et al.* (2004) *Phys. Fluids* ***17:****053301*

What, another gel model?

$$\boldsymbol{\sigma} = -p\mathbf{I} + \boldsymbol{\sigma}_{\mathrm{eff}}$$
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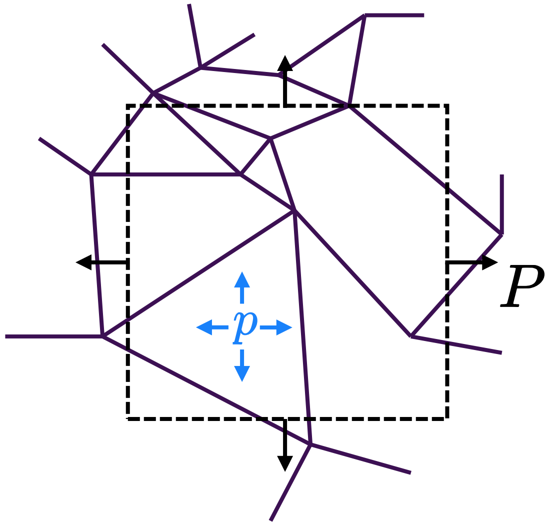
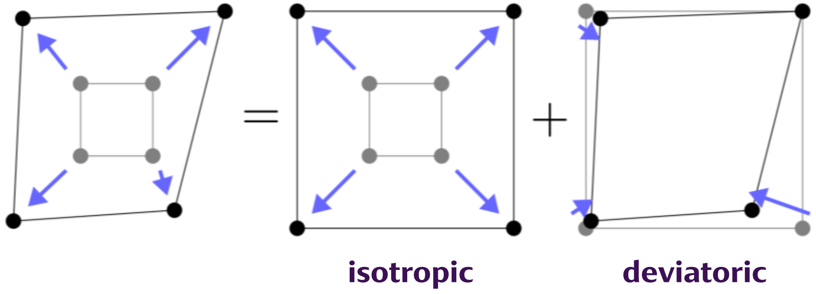


Linear (Biot) poroelasticity specifies a linear-elastic constitutive relation linking strains to effective stresses.

Hydrogels swell a lot, with potentially large strains: linear is no good!

One way around this: use **finite strain (nonlinear) elastic models** for effective stress.

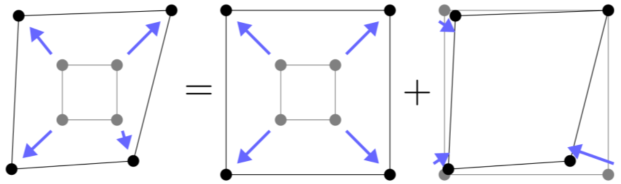
e.g. Hencky model $\boldsymbol{\sigma}_{\mathrm{eff}} = \dfrac{\Lambda\phi}{2}\,\mathrm{tr}\big(\ln(\mathbf{F}\mathbf{F}^{\mathrm{T}})\big)\mathbf{I} + \dfrac{M-\Lambda}{2}\ln(\mathbf{F}\mathbf{F}^{\mathrm{T}})$



Biot (1941) *J. Appl. Phys.* ***12:****155-164*; Tanaka *et al.* (1973) *J. Chem Phys.* ***59:****5151-5159*; MacMinn *et al.* (2016) *Phys. Rev. Appl.* ***5:****044020*

Linear-elastic-nonlinear-swelling (LENS)

$$\boldsymbol{\sigma} = -p\mathbf{I} + \boldsymbol{\sigma}_{\text{eff}}$$
$$P = p + \Pi$$



<u>Key idea</u>: assume linearity only in the **deviatoric strain** from some **fully-swollen reference state** $\phi \equiv \phi_0$

Therefore, the deviatoric part of $\boldsymbol{\sigma}_{\text{eff}}$ must depend linearly on the deviatoric part of the Cauchy strain (the isotropic part could be huge)

$$\mathbf{e} = \frac{1}{2}\left[(\nabla\boldsymbol{\xi}) + (\nabla\boldsymbol{\xi})^{\mathsf{T}}\right] = \left[1 - \left(\frac{\phi}{\phi_0}\right)^{1/3}\right]\mathbf{I} + \boldsymbol{\epsilon}$$

isotropic strain
depends only on degree to which gel is swollen

deviatoric strain
assumed small

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

shear modulus depends on swelling!
dry gels will probably be stiffer

isotropic part must be (-) osmotic pressure
since the isotropic part of the total stress tensor is (-) the bulk pressure

depends on swelling alone
isotropic strains lead to isotropic stresses – see the isotropic part of strain tensor

physically intuitive result

JJW & Worster (2023) *J. Fluid Mech.* ***960:***A37

Linear-elastic-nonlinear-swelling (LENS)

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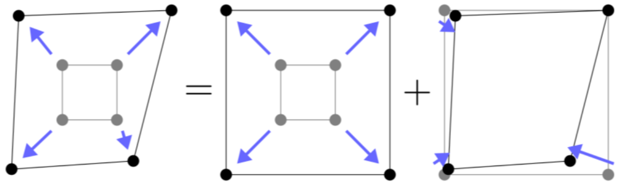


$$\mathbf{e} = \frac{1}{2}\left[(\boldsymbol{\nabla\xi}) + (\boldsymbol{\nabla\xi})^{\mathsf{T}}\right] = \left[1 - \left(\frac{\phi}{\phi_0}\right)^{1/3}\right]\mathbf{I} + \boldsymbol{\epsilon}$$

$$\boldsymbol{\sigma}_{\text{eff}} = -\Pi(\phi)\mathbf{I} + 2\mu_s(\phi)\boldsymbol{\epsilon}$$
$$\boldsymbol{u} = (1-\phi)(\boldsymbol{u_w} - \boldsymbol{u_p})$$
$$\boldsymbol{q} = (1-\phi)\boldsymbol{u_w} + \phi\boldsymbol{u_p}$$

- Have an expression for stress in the gel, so conservation of momentum links pressure gradients to deviatoric strains,

$$\boldsymbol{\nabla}\cdot\boldsymbol{\sigma} = 0 \quad \text{so} \quad \underbrace{\boldsymbol{\nabla}p = -\boldsymbol{\nabla}\Pi(\phi)}_{} + 2\boldsymbol{\nabla}\cdot[\mu_s(\phi)\boldsymbol{\epsilon}]$$

pervadic pressure gradients
oppose osmotic ones

- Since gradients in pervadic pressure drive flows, this allows us to describe gel reconfiguration (when coupled with conservation of polymer and water)

$$\frac{\partial\phi}{\partial t} + \boldsymbol{q}\cdot\boldsymbol{\nabla}\phi = \boldsymbol{\nabla}\cdot(\phi\boldsymbol{u}) \qquad \text{alongside} \qquad \boldsymbol{u} = -\frac{k(\phi)}{\mu_l}\boldsymbol{\nabla}p$$

depends on swelling

phase-averaged (gel and water) flux

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

JJW & Worster (2023) *J. Fluid Mech.* ***960:****A37*; JJW *et al.* (2023) *J. Fluid Mech.* ***960:****A38*

Characterising a gel

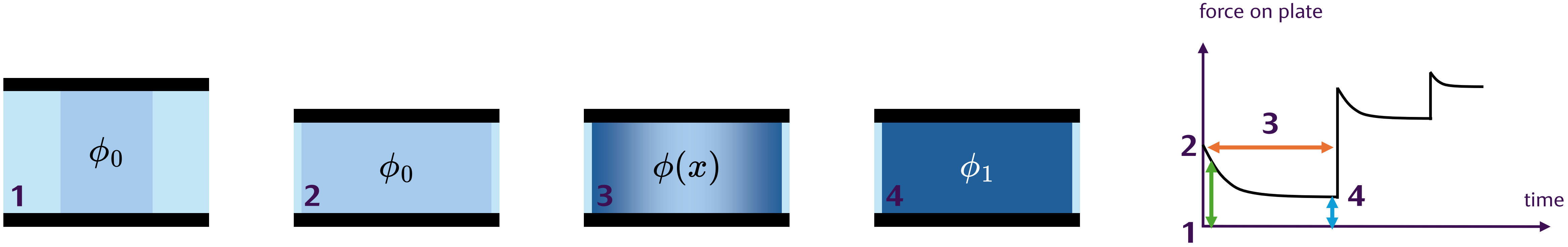
$$\frac{\partial\phi}{\partial t} + \boldsymbol{q}\cdot\boldsymbol{\nabla}\phi = \boldsymbol{\nabla}\cdot\left\{\frac{k(\phi)}{\mu_l}\left[\phi\frac{\partial\Pi}{\partial\phi} + \frac{4\mu_s(\phi)}{3}\left(\frac{\phi}{\phi_0}\right)^{1/3}\right]\boldsymbol{\nabla}\phi\right\}$$

$$\boldsymbol{\sigma} = -[p + \Pi(\phi)]\mathbf{I} + 2\mu_s(\phi)\boldsymbol{\epsilon} \qquad \boldsymbol{u} = \frac{k(\phi)}{\mu_l}\left[\frac{\partial\Pi}{\partial\phi} + \frac{4\mu_s(\phi)}{3\phi}\left(\frac{\phi}{\phi_0}\right)^{1/3}\right]\boldsymbol{\nabla}\phi$$

Shear modulus characterises the stiffness of a hydrogel and describes the initial elastic response before water diffuses through the structure

Osmotic pressure characterises the affinity for water ('desire' to swell or deswell)

Permeability describes the resistance to viscous flow through the pore scaffold



JJW & Worster (2023) *J. Fluid Mech.* ***960:***A37; JJW *et al.* (2023) *J. Fluid Mech.* ***960:***A38; JJW (2024) *PhD thesis, U. Cambridge*

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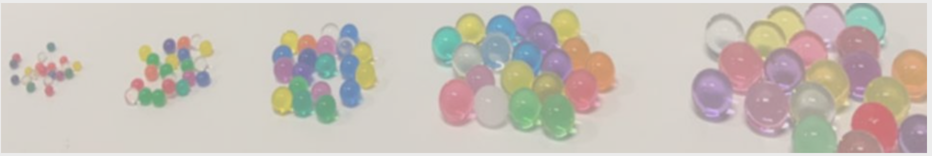

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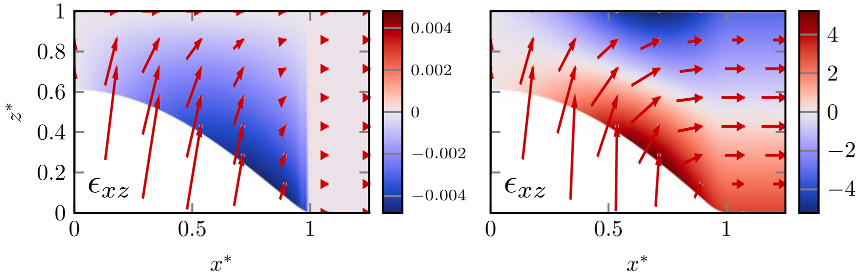

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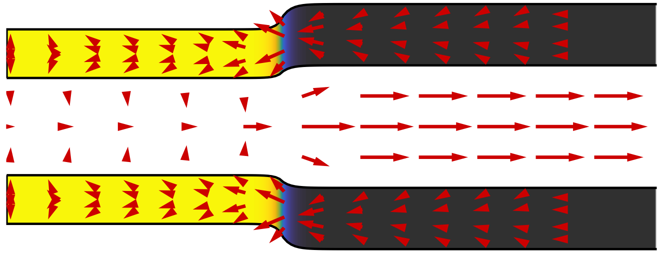
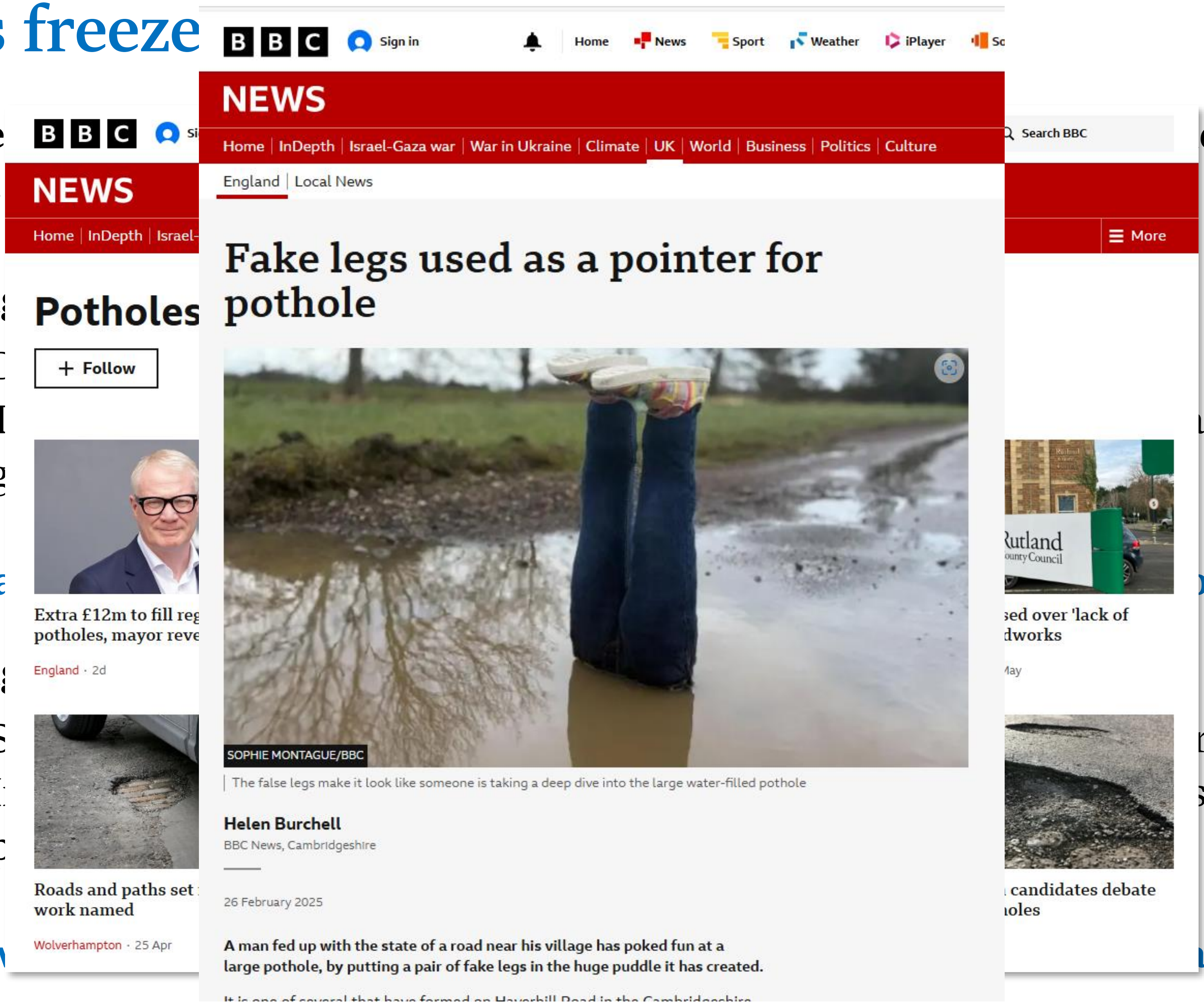


How do gels freeze

What brings me he … d provides insight into analogous materials


Journal of the Mechanics and Physics of Solids

Characterizing hydrogel behavior under compression with gel-freezing osmometry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Roads and paths set … work named

Wolverhampton · 25 Apr

… candidates debate …oles

Fake legs used as a pointer for pothole

SOPHIE MONTAGUE/BBC

The false legs make it look like someone is taking a deep dive into the large water-filled pothole

Helen Burchell

BBC News, Cambridgeshire

26 February 2025

A man fed up with the state of a road near his village has poked fun at a large pothole, by putting a pair of fake legs in the huge puddle it has created.

Insi…

- I…
- T… g… …ry until ice no longer

Wha… …-scale effects.


SCIENCE ADVANCES | RESEARCH ARTICLE

Dehydration drives damage in the freezing of brittle hydrogels

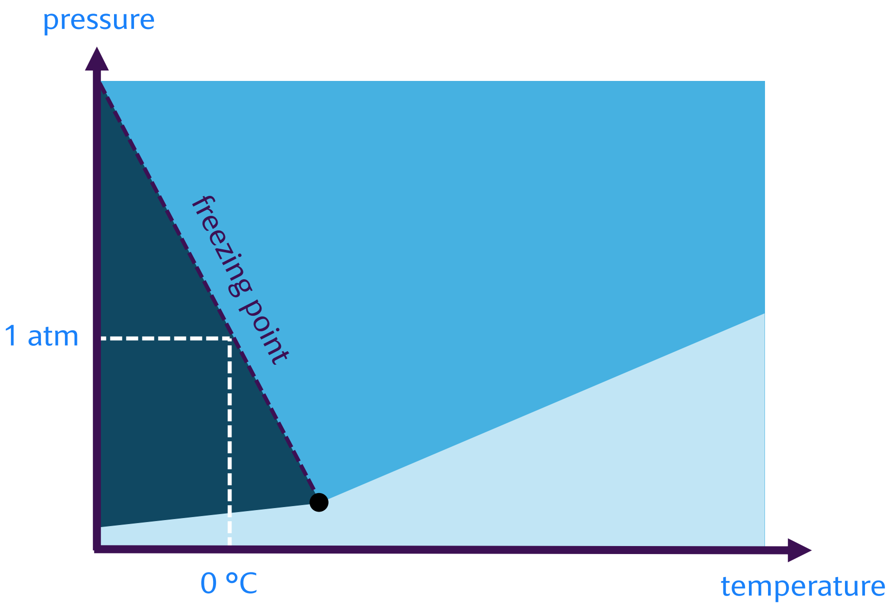
Insi…

- S… …rmal expansion of ice
- I… p… …, displaces the

How … …bout fluid flows?

Yang *et al.* (2024) *Sci. Adv.* **10:***eado7750*; Feng *et al.* (2025) *J. Mech. Phys. Solids* **201:***106166*

Why don't gels freeze?



Pressure is raised inside the pore spaces owing to capillarity, so the *ice-entry temperature* is modified by the Gibbs-Thompson relation

(neither actually derived this...)

$$T_{IE} = T_m \left[1 - \frac{\gamma\kappa}{\rho_{\text{ice}}\mathcal{L}} \right]$$

surface tension and average pore curvature

equilibrium freezing temperature (~273 K)

specific latent heat of fusion

This depresses the freezing point of water inside the pores. At a boundary, water will still want to freeze into ice.

At the boundary, the temperature is given by the Clausius-Clapeyron relation:

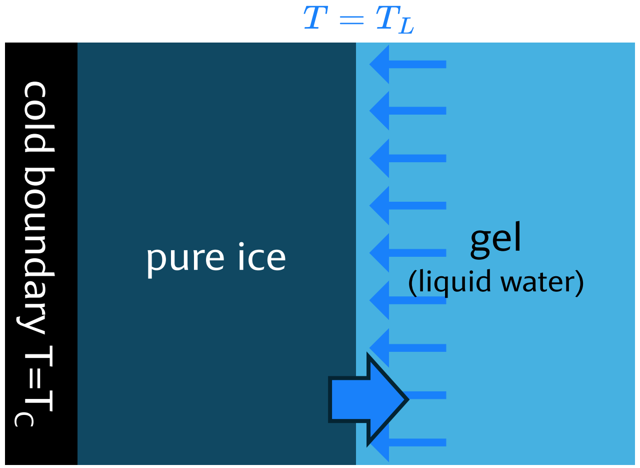
(...ditto)

$$\mathcal{L}\frac{T_L - T_m}{T_m} = \frac{\boldsymbol{n}\cdot\boldsymbol{\sigma}\cdot\boldsymbol{n} + p_{\text{atm}}}{\rho_{\text{ice}}} - \frac{p_{\text{gel}} - p_{\text{atm}}}{\rho_{\text{water}}}$$

$$\rho_{\text{water}}\mathcal{L}\frac{T_L - T_m}{T_m} = p_{\text{gel}} - p_{\text{atm}} = p_{\text{gel}} + \boldsymbol{n}\cdot\boldsymbol{\sigma}\cdot\boldsymbol{n} = -\Pi(\phi)$$

equals (-) bulk pressure

assume no overburden stress $\boldsymbol{n}\cdot\boldsymbol{\sigma}\cdot\boldsymbol{n} = -p_{\text{atm}}$



Worster (2000) *in* Perspectives in Fluid Dynamics *Cambridge Uni. Press*; Style *et al.* (2023) *J. Glaciol.* ***69:****1091-1096*

Putting ice in our gel model

$T_{IE} < T_L < T_m$

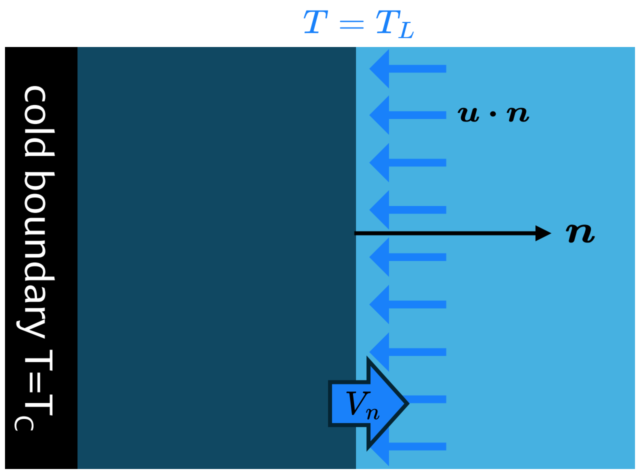
$$T_L = T_m \left[1 - \frac{\Pi(\phi)}{\rho_{\text{water}} \mathcal{L}} \right]$$

As a boundary condition on polymer fraction this sets the value of the osmotic pressure, and hence the amount of deswelling, given a liquidus temperature on the interface

As a boundary condition on temperature this sets a lower freezing point at the interface when the gel is drier

This alone doesn't quite close the model:

- Mass is conserved $\rho_{\text{ice}} V_n = -\rho_{\text{water}} \boldsymbol{u} \cdot \boldsymbol{n}$
- Stefan condition (energy is conserved) $\rho_{\text{ice}} \mathcal{L} V_n = -[\mathcal{K}(\boldsymbol{n} \cdot \boldsymbol{\nabla} T)]_{\text{ice}}^{\text{gel}}$



JJW & Worster (2025) *Proc. Roy. Soc. A* ***481:****20240721*

Gel-freezing osmometry

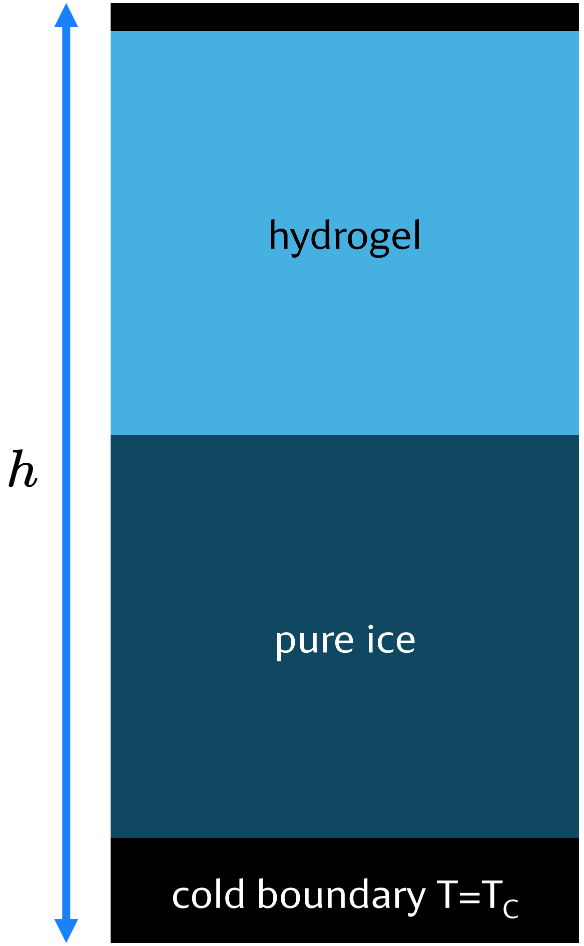
$$T_L = T_m \left[1 - \frac{\Pi(\phi)}{\rho_{\text{water}}\mathcal{L}}\right] \qquad \rho_{\text{ice}}\mathcal{L}V_n = -[\mathcal{K}(\boldsymbol{n}\cdot\boldsymbol{\nabla}T)]_{\text{ice}}^{\text{gel}} \qquad \rho_{\text{ice}}V_n = -\rho_{\text{water}}\boldsymbol{u}\cdot\boldsymbol{n}$$

Consider the 1D problem with an insulated lid and a cold boundary, initially with no ice and a fully-swollen gel

Eventually a steady state is reached. No heat fluxes, no more growth of ice, thus no fluid fluxes

- No heat fluxes: $T \equiv T_C = T_L$
- No fluid fluxes: $\phi \equiv \phi_C$ with $\phi_C(h - a_\infty) = \phi_0 h$

$$\Pi\left(\frac{\phi_0 h}{h - a_\infty}\right) = \rho_{\text{water}}\mathcal{L}(T_m - T_C)$$



Feng *et al.* (2025) *J. Mech. Phys. Solids* ***201:****106166*; JJW & Worster (2025) *Proc. Roy. Soc. A* ***481:****20240721*

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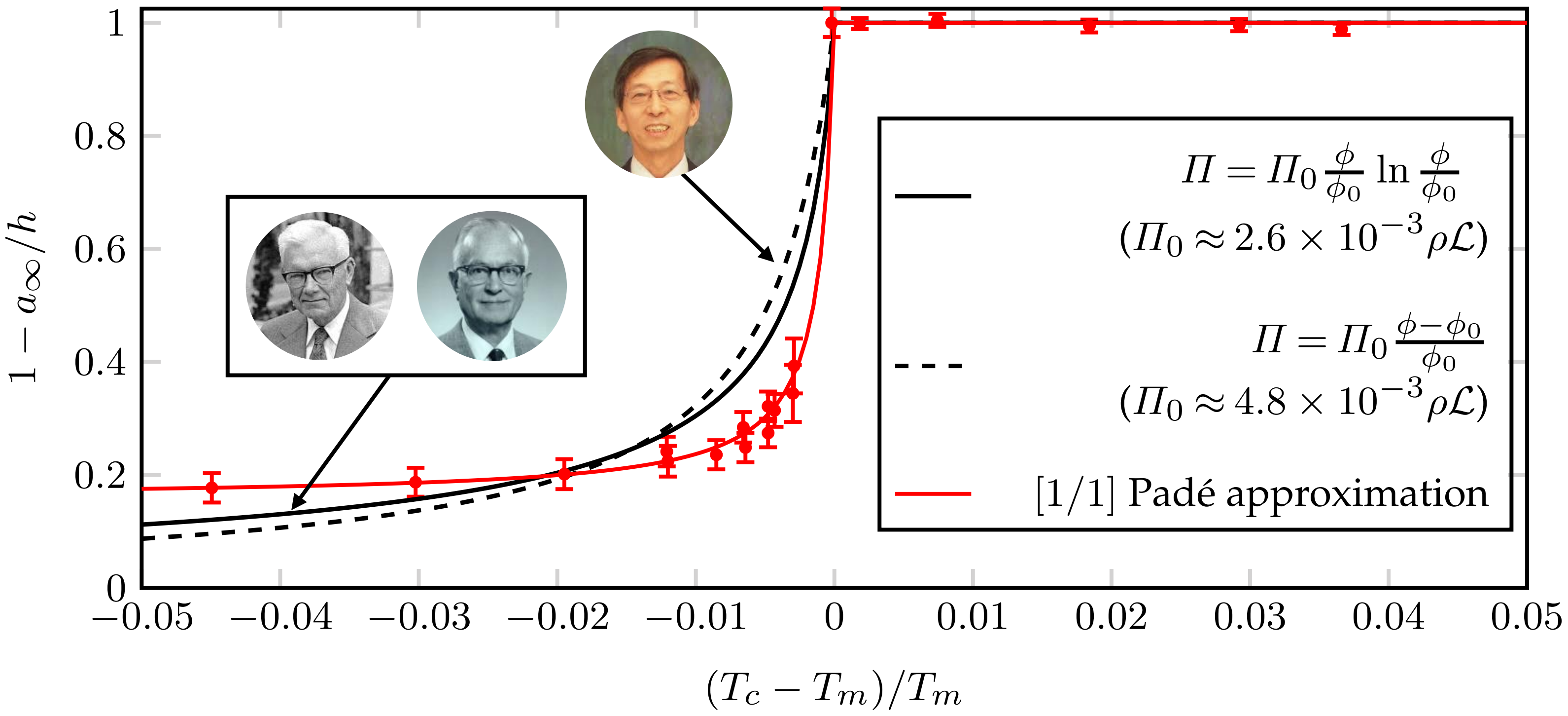


$= \rho$

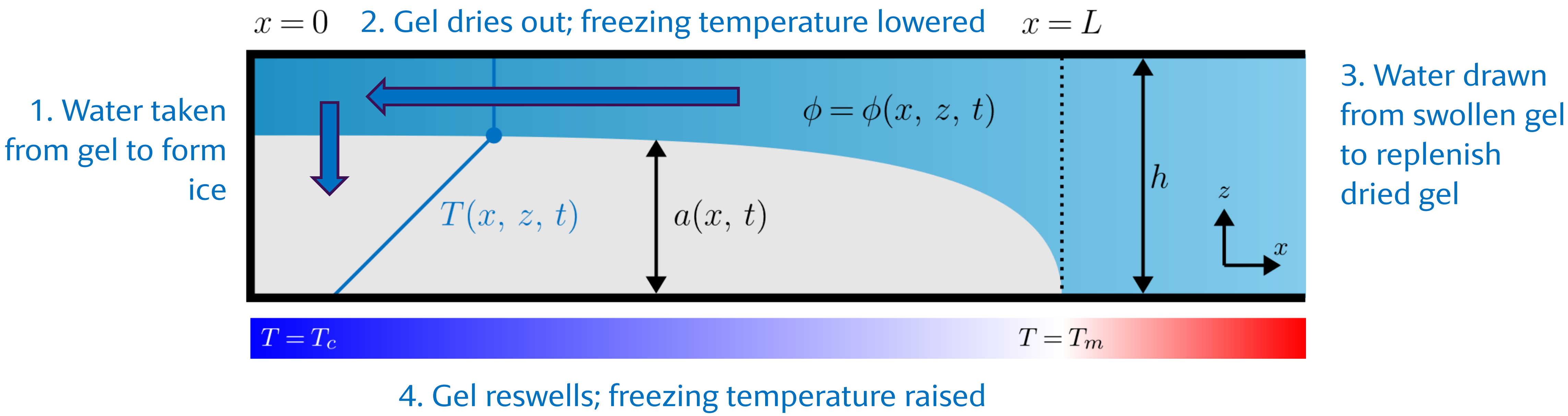
$$\Pi\left(\frac{\phi_0 h}{h - a_\infty}\right) = \rho_{\text{water}} \mathcal{L}(T_m - T_C)$$

$$\Pi(\phi) = \frac{10^{-3}\rho\mathcal{L}}{\phi_0} \frac{\phi - \phi_0}{1 - \phi/(6.6\phi_0)}$$

Feng *et al.* (2025) *J. Mech. Phys. Solids* ***201:****106166*; JJW & Worster (2025) *Proc. Roy. Soc. A* ***481:****20240721*

Modelling the (transient) freezing process

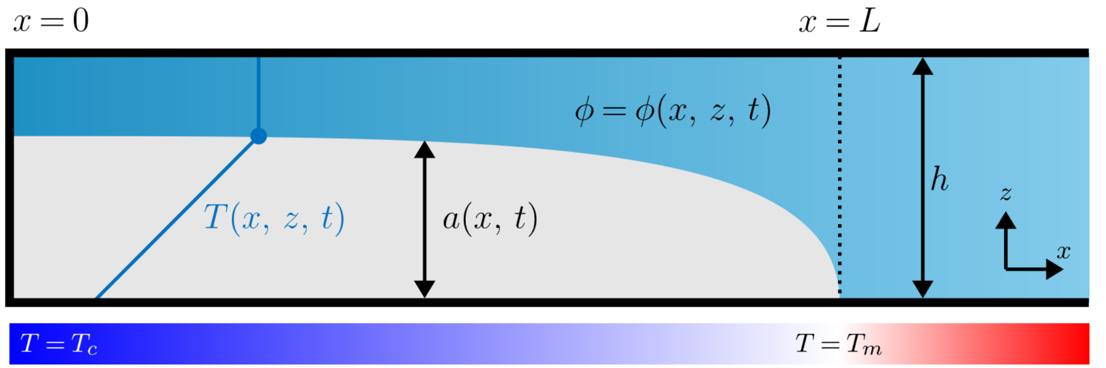
So far, we have **only considered the final steady state** in freezing experiments; LENS brings us no real advantages here. To see its real use, we consider a more complicated physical setup.



- Ice grows vertically from the base but **to differing extents**
- Water drawn vertically downwards from the gel **and also horizontally** to replenish partially-dried gel

Yang *et al.* (2024) *Sci. Adv.* ***10:****eado7750*; JJW & Worster (2025) *Proc. Roy. Soc. A* ***481:****20240721*

Building a mathematical model



Temperature field

$$\frac{\partial T}{\partial t}=\kappa_{\text{ice}}\nabla^2 T \quad \text{and} \quad \frac{\partial T}{\partial t}=\kappa_{\text{gel}}\nabla^2 T$$

Gel composition

$$\frac{\partial \phi}{\partial t}+\boldsymbol{q}\cdot\boldsymbol{\nabla}\phi+\boldsymbol{\nabla}\cdot\left[\frac{\phi k(\phi)}{\mu_l}\boldsymbol{\nabla}p\right]=0 \quad \text{with} \quad \boldsymbol{\nabla}p+\boldsymbol{\nabla}\Pi=2\boldsymbol{\nabla}\cdot[\mu_s(\phi)\boldsymbol{\epsilon}]$$

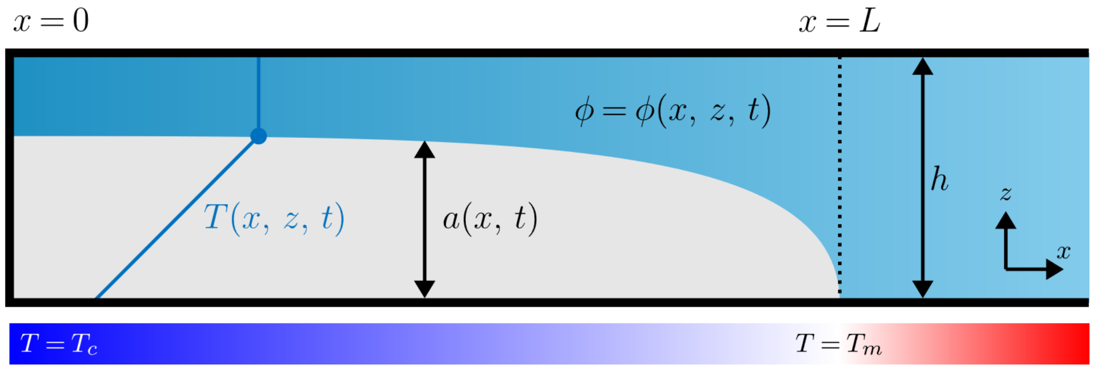
Ice growth

$$\rho\mathcal{L}\frac{\mathrm{d}a}{\mathrm{d}t}=-\left[\mathcal{K}\left(\frac{\partial T}{\partial z}-\frac{\partial a}{\partial x}\frac{\partial T}{\partial x}\right)\right]_{\text{ice}}^{\text{gel}} \qquad T|_{z=a(x,\,t)}=T_m\left[1-\frac{\Pi(\phi)}{\rho\mathcal{L}}\right]$$

- **Assume the channel is slender** so $\varepsilon=h/L\ll 1$
- Take the limit of a **large Lewis number**; heat diffuses much faster than water through polymer

JJW & Worster (2025) *Proc. Roy. Soc. A* ***481:****20240721*

Building a mathematical model



$$T = T_m - \frac{1}{2}(T_m - T_C)\left(1 + \cos\frac{\pi x}{L}\right) \qquad T = T_m \; (x \geq L)$$

Temperature field

- Linear in the ice
- Constant (equal to liquidus) in the gel
- Set by degree of deswelling

Gel composition

Neumann boundary conditions on walls. Polymer fraction set by liquidus temperature on ice-gel boundary.

$$\frac{\partial \phi}{\partial t} + \left(\frac{\phi}{\phi_0}\right)^{-1/2}\frac{\partial \xi}{\partial t}\frac{\partial \phi}{\partial x} + \left(\frac{\phi}{\phi_0}\right)^{-1/2}\frac{\partial \eta}{\partial t}\frac{\partial \phi}{\partial z} = \frac{k(\phi)}{\mu_l}\frac{\partial}{\partial \phi}\left[\Pi(\phi) + 2\mu_s(\phi)\left(\frac{\phi}{\phi_0}\right)^{1/2}\right]\frac{\partial^2 \phi}{\partial z^2}$$

$\boldsymbol{\xi} = (\xi, \eta)$

Ice growth

thermal conductivity

osmotic depression

$$\frac{\mathrm{d}}{\mathrm{d}t}(a^2) = \frac{\mathcal{K}}{\rho \mathcal{L}}\left[(T_m - T_C)\left(1 + \cos\frac{\pi x}{L}\right) - \frac{2\Pi(\phi)}{\rho \mathcal{L}}\right]$$

energy stored by making new ice

undercooling

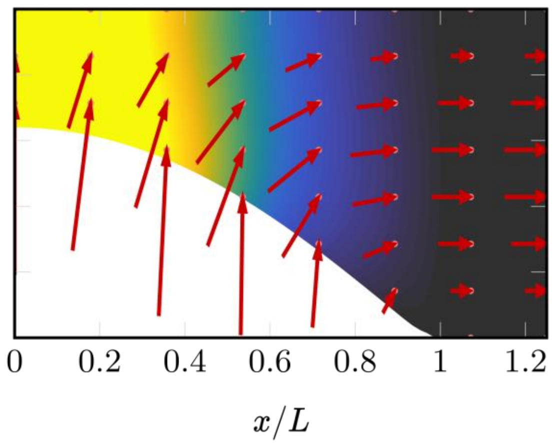
JJW & Worster (2025) *Proc. Roy. Soc. A* ***481:**20240721*

Where does the gel go?

No-slip boundary conditions

$$\xi = -\frac{1}{2\mu_s}\frac{\partial P}{\partial x}(h-z)(z-a)$$

$$\eta = 2\int_z^h \left[(\phi/\phi_0)^{1/2} - 1\right] \mathrm{d}z' + \frac{(h-z)^2}{12\mu_s}\left[\frac{\partial^2 P}{\partial x^2}(h+2z-3a) - 3\frac{\partial P}{\partial x}\frac{\partial a}{\partial x}\right]$$

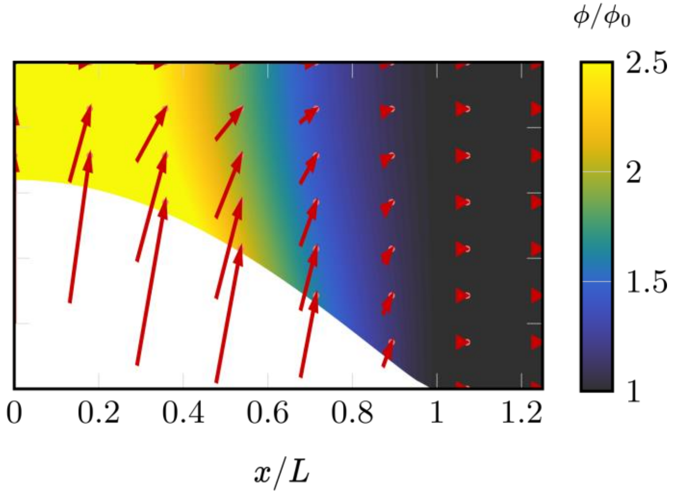


- Parabolic horizontal displacement profile
- Requires stiff gel *and* little drying or else deviatoric strains are large

Free-slip boundary conditions

$$\xi = \int_0^x \left\{\frac{a}{h-a} - \frac{2}{h-a}\int_a^h \left[(\phi/\phi_0)^{1/2} - 1\right] \mathrm{d}z'\right\} \mathrm{d}x'$$

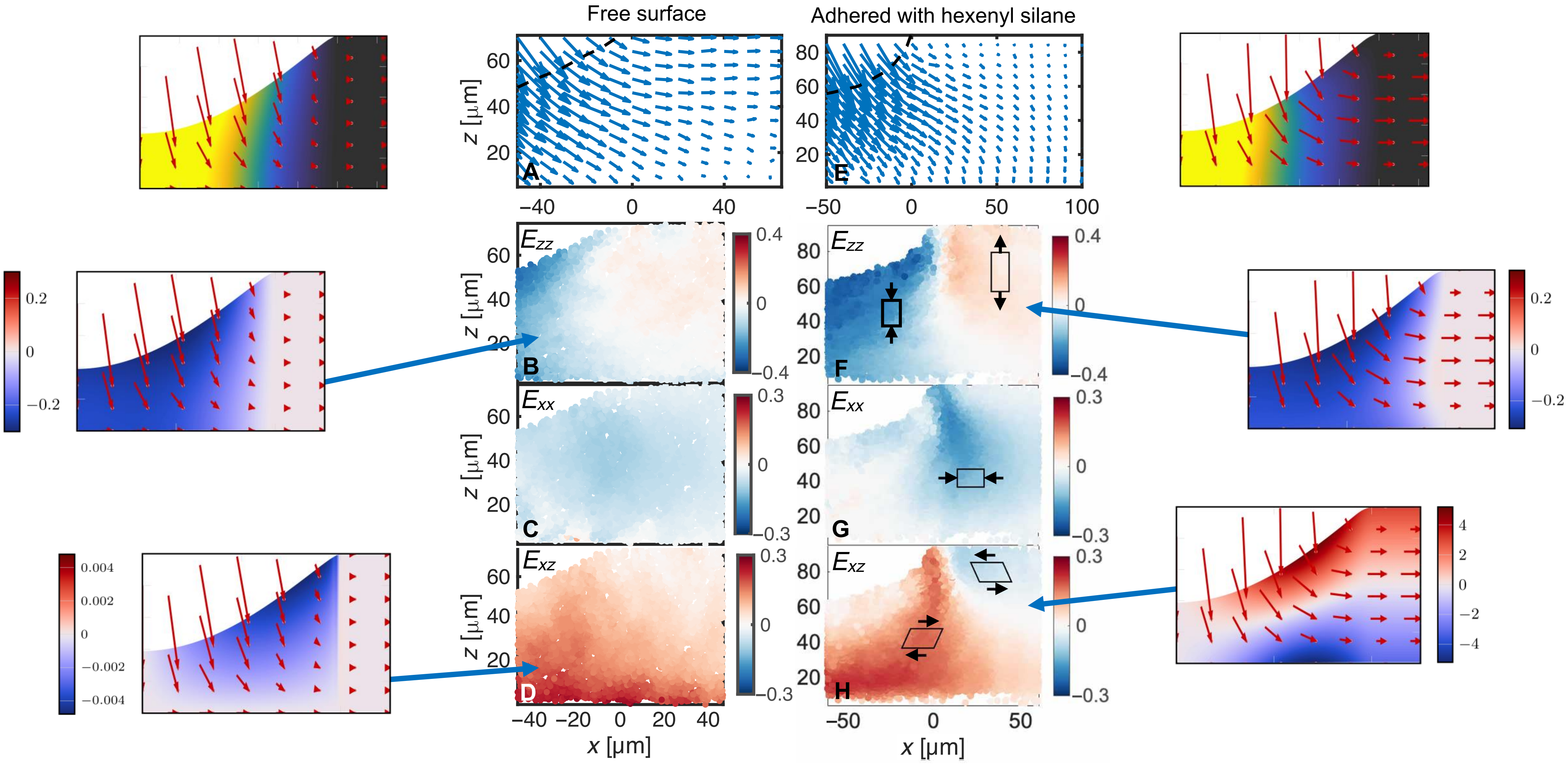
$$\eta = 2\int_z^h \left[(\phi/\phi_0)^{1/2} - 1\right] \mathrm{d}z' + \frac{h-z}{h-a}\left\{a - 2\int_a^h \left[(\phi/\phi_0)^{1/2} - 1\right] \mathrm{d}z'\right\}$$



- ‘Stretched-plug’ horizontal displacement
- Requires little drying or else deviatoric strains are large, but gel can be stiff

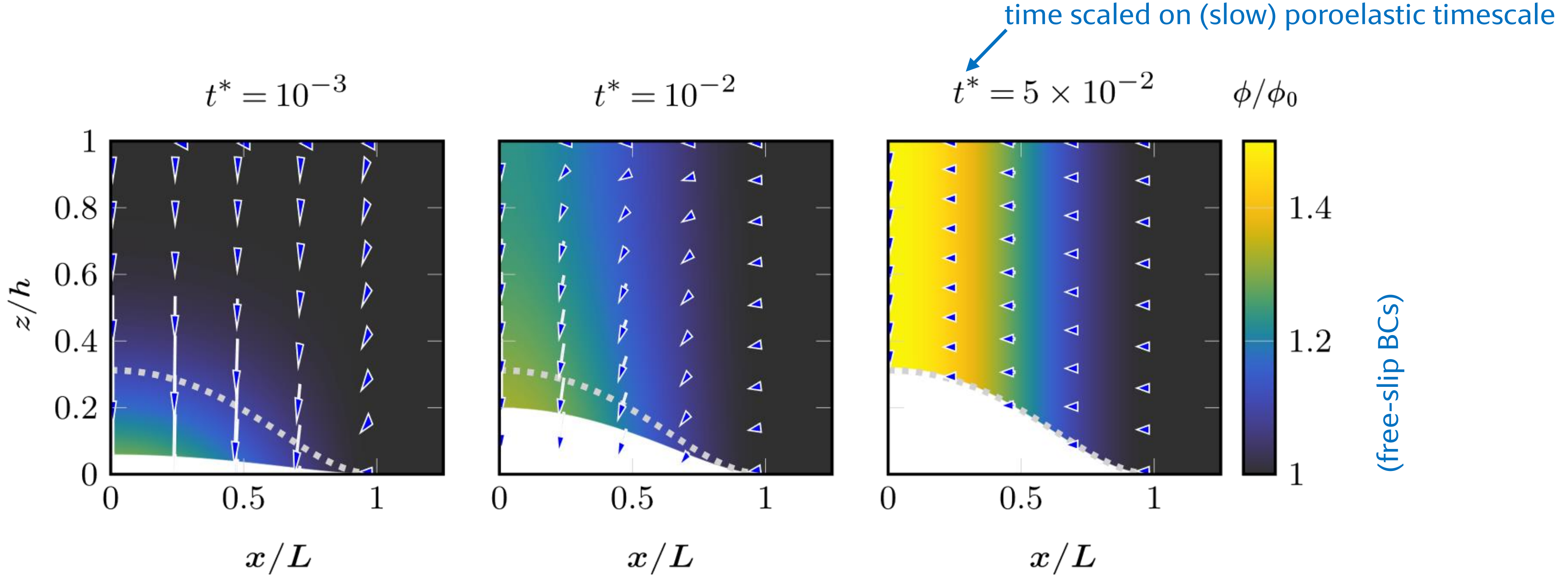
Yang *et al.* (2024) *Sci. Adv.* ***10:****eado7750*; JJW & Worster (2025) *Proc. Roy. Soc. A* ***481:****20240721*

Stress buildup in hydrogels



Yang *et al.* (2024) *Sci. Adv.* ***10:****eado7750*; JJW & Worster (2025) *Proc. Roy. Soc. A* ***481:****20240721*

Where does the water go?



- Initially, the gel remains swollen and all water flows are vertically downwards: $a \approx \sqrt{\frac{\mathcal{K}}{\rho \mathcal{L}}(T_m - T_C)\left(1 + \cos\frac{\pi x}{L}\right) t}$
- Eventually, osmotic effects begin to play a role and water is drawn from more swollen regions into drier parts of the gel
- Finally, a steady state is reached where there is no further growth of ice

JJW & Worster (2025) *Proc. Roy. Soc. A* ***481:****20240721*

When does it all stop?

- As in the unidirectional case, freezing stops when there are no heat fluxes from the ice

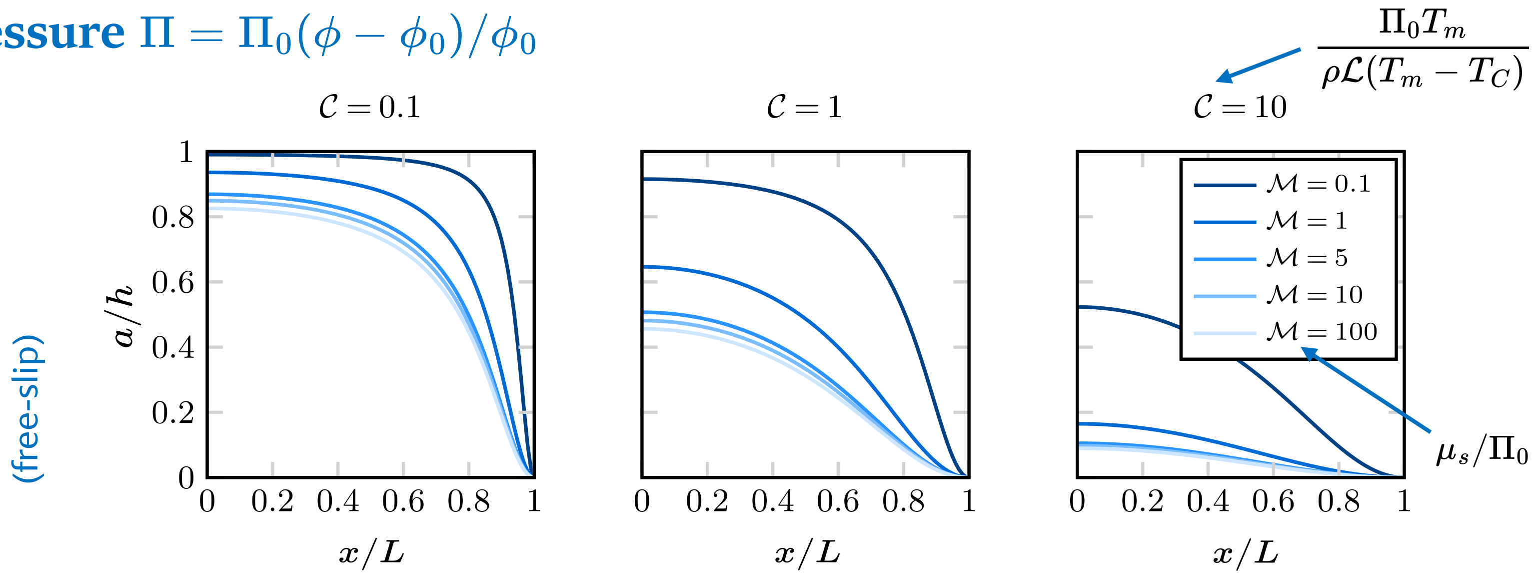
$$\rho\mathcal{L}\frac{\mathrm{d}a}{\mathrm{d}t} = -\left[\mathcal{K}\left(\frac{\partial T}{\partial z} - \frac{\partial a}{\partial x}\frac{\partial T}{\partial x}\right)\right]_{\mathrm{ice}}^{\mathrm{gel}}$$

gel sits on liquidus

slenderness approximation

- This gives $\phi = \phi_\infty(x)$ with $\Pi(\phi_\infty) = \frac{\rho\mathcal{L}}{2}\left(1 - \frac{T_C}{T_m}\right)\left(1 + \cos\frac{\pi x}{L}\right)$
- Need deviatoric stresses to balance these osmotic pressures *exactly* or else there is flow

Linear osmotic pressure $\Pi = \Pi_0(\phi - \phi_0)/\phi_0$

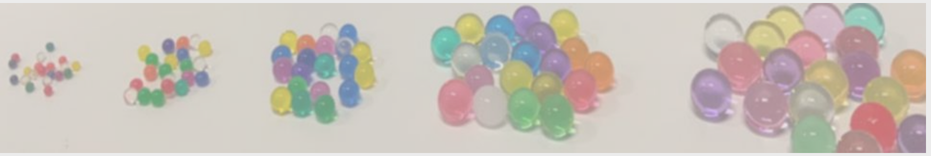


JJW & Worster (2025) *Proc. Roy. Soc. A* ***481:****20240721*

Overview

1. Thinking about gels like a mathematician

Osmosis · elastic stresses · equilibrium swelling · transport of water · shape change in swelling/drying · behaviour at interfaces · characterising a gel

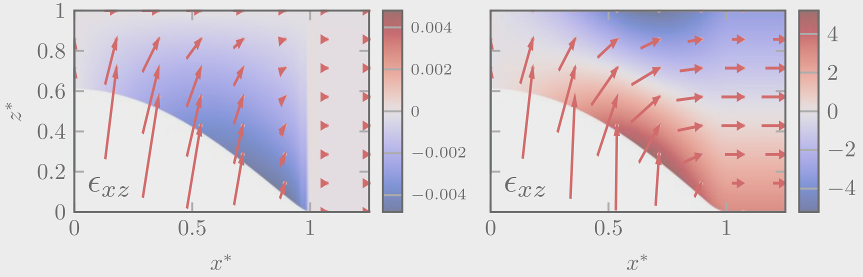


Temperature (representative values)

270 K — 300 K — 310 K

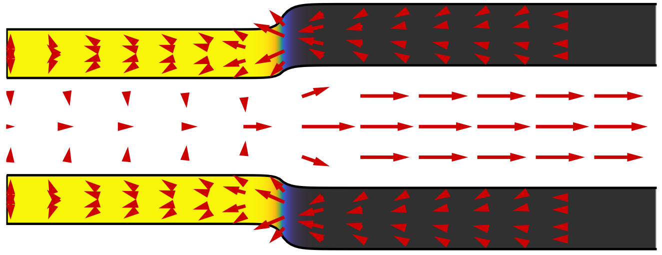
2. Freezing hydrogels at low*(-ish)* temperatures

Formation of pure ice · cryosuction · applying our model to GelFrO · a 2D model · stress buildup



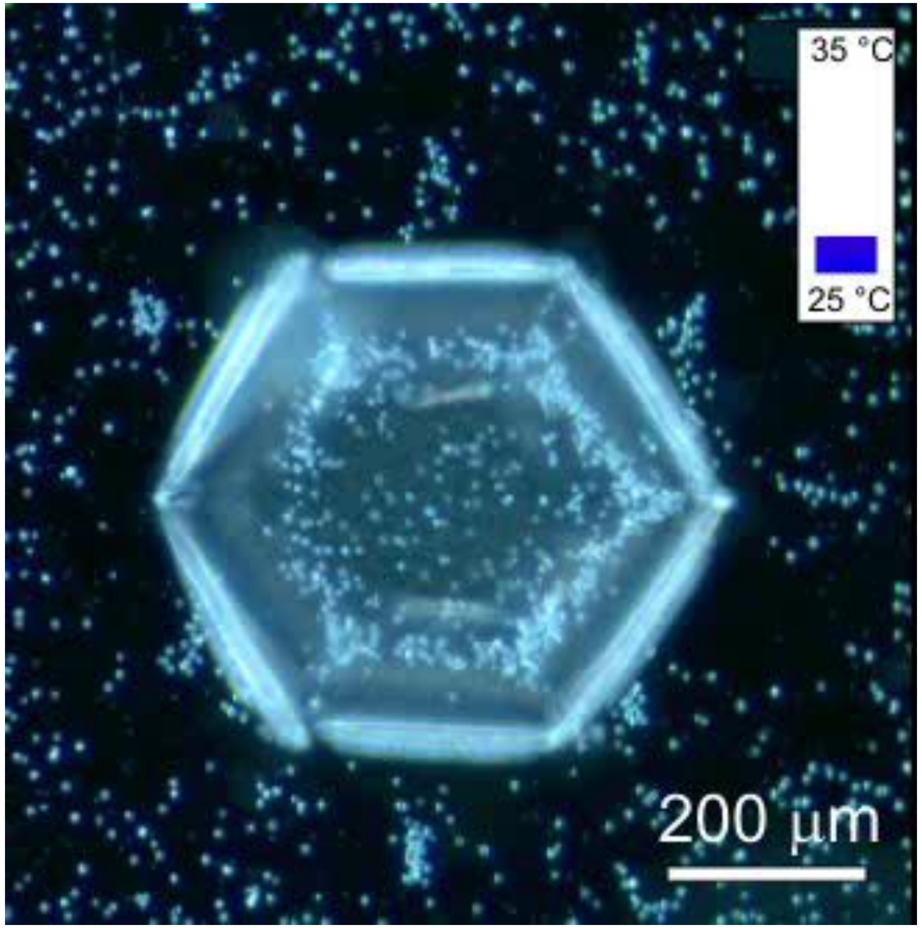
3. Building with thermo-responsive gels

Heating effects on swelling · heat transfer in gels · building pumps with collapsing tubes



Thermo-responsive hydrogels

Some gels, like many based on poly(N-isopropylacrylamide) (pNIPAM) undergo a transition at a critical temperature called the **Lower Critical Solution Temperature (LCST)**



Qualitatively, it appears that there is a new equilibrium (dry) polymer state above the LCST, with transition between the two states slow, mediated by diffusion of water

$$\phi_0 = \begin{cases} \phi_{00} & T \leq T_C \\ \phi_{0\infty} & T > T_C \end{cases}$$

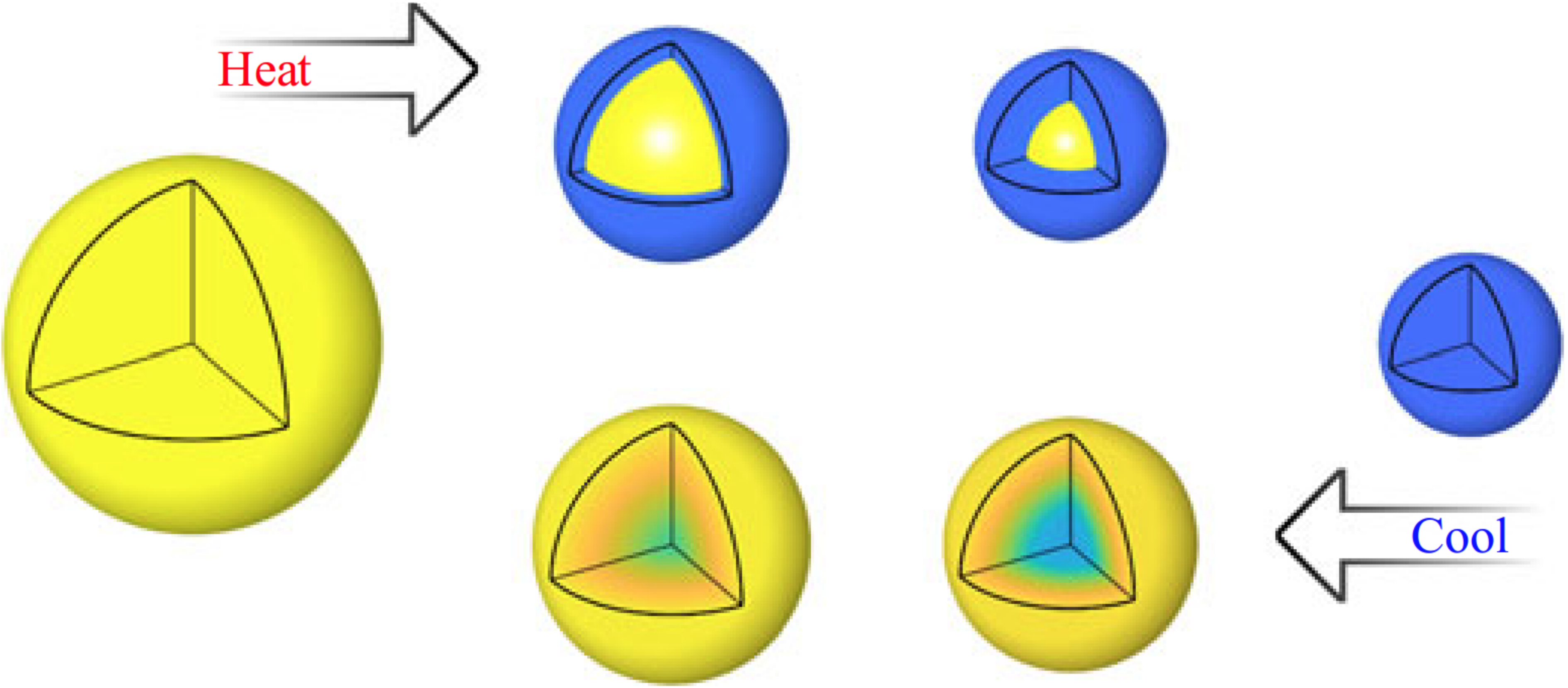
$$\mathcal{W} = \frac{k_B T}{2\Omega_p}\left[\mathrm{tr}\left(\mathbf{F_d}\,\mathbf{F_d^T}\right) - 3 + 2\log\phi\right] + \frac{k_B T}{\Omega_f}\left[\frac{1-\phi}{\phi}\log(1-\phi) + \chi(\phi, T)(1-\phi)\right]$$

Solving the implicit relation $\left.\frac{\partial \mathcal{W}}{\partial \phi}\right|_{\phi=\phi_0} = 0$ gives the equilibrium polymer fraction as a function of temperature if we know the interaction parameter's value

Stoychev *et al.* (2011) *Soft Matter* ***7:****3277-3279*

Thermo-responsive hydrogels

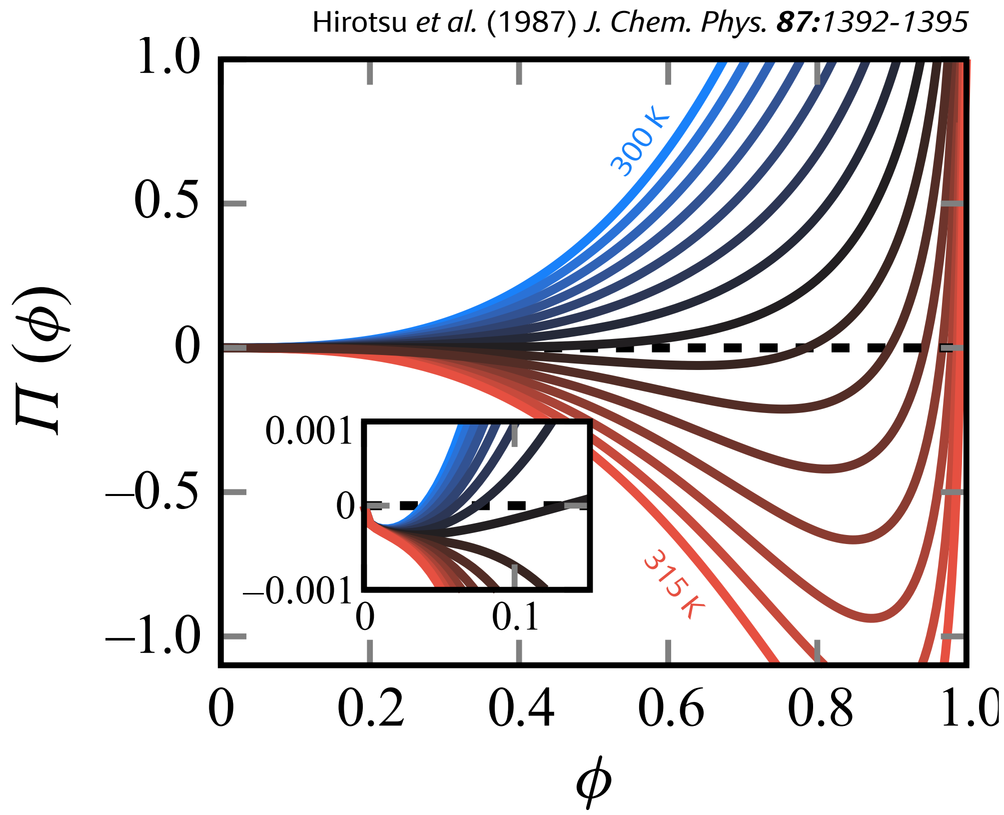
Take a simple functional form $\chi(\phi, T) = A_0 + A_1 T + (B_0 + B_1 T)\phi + \mathcal{O}(T^2, \phi^2)$



...we're skipping out some significant and important behaviour here, however.

Butler & Montenegro-Johnson (2022) *J. Fluid Mech.* ***947:****A11*

Thermo-responsive hydrogels



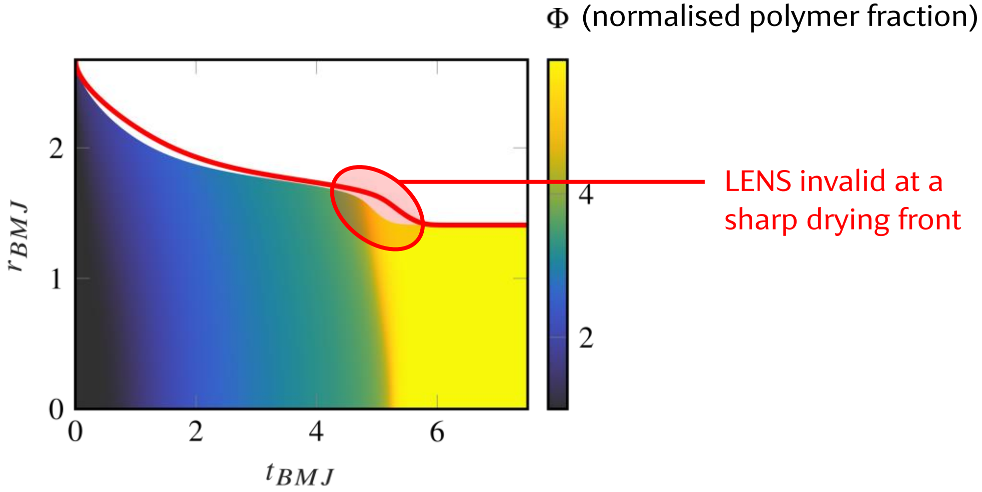
motivating our choice $\phi_0 = \begin{cases} \phi_{00} & T \leq T_C \\ \phi_{0\infty} & T > T_C \end{cases}$

If the same parameter set is used to generate a generalised osmotic pressure (in the LENS formalism), we see the same rapid switch in equilibrium values as the temperature increases

Phenomenologically, it suffices to take

$$\Pi(\phi) = \Pi_0 \frac{\phi - \phi_0(T)}{\phi_0(T)}$$

Big question: Does this work?



JJW & Montenegro-Johnson (2025) *J. Fluid Mech.* ***1009:****A38*

Heat transfer in thermo-responsive gels

How about cases where heat is evolving in a gel, close to the LCST? How is heat transferred and how can deswelling or reswelling feed back into this?

Internal energy can change *via*:

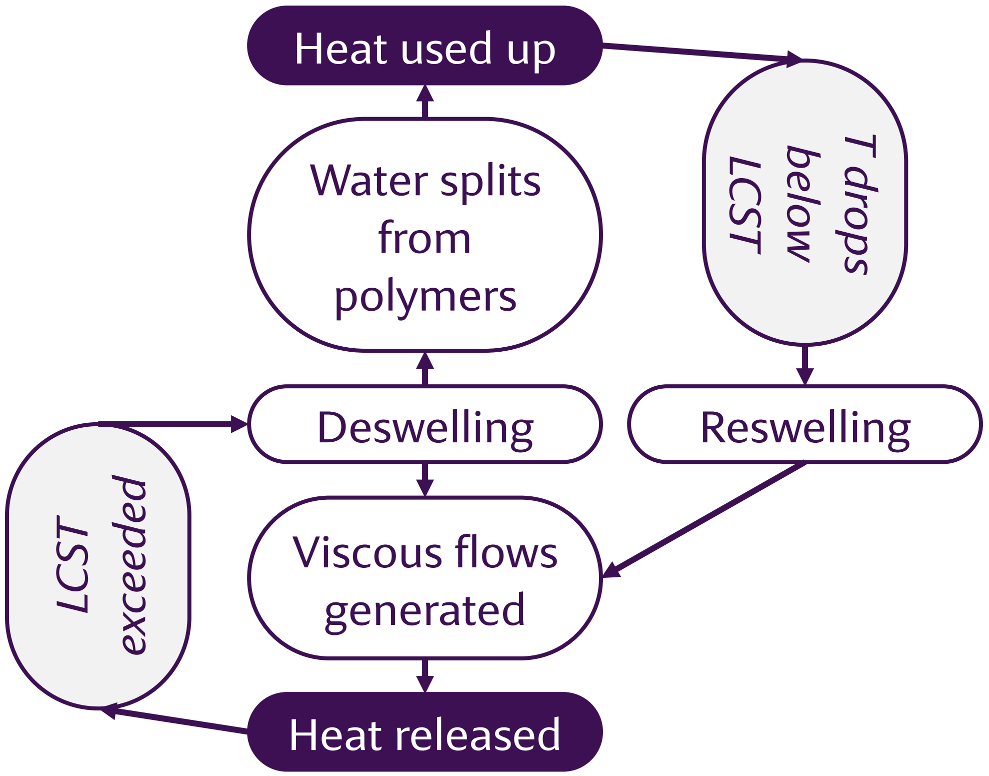
1. **External supply of heat** *easy to neglect in most cases*

2. **Heat generation due to viscous flows**
   As gels swell or deswell and water is driven through the scaffold, frictional effects can generate heat. Positive feedback

3. **Heat transfer by advection**
   Both in the solid and liquid phases

4. **Heat transfer by diffusion**

5. **Energy used in swelling or drying**
   Breaking water molecules away from polymer chains uses energy, and vice versa. Negative feedback



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Heat transfer in thermo-responsive gels

1. External supply of heat
2. Heat generation due to viscous flows
3. Heat transfer by advection
4. Heat transfer by diffusion
5. Energy used in swelling or drying

Full derivation in JJW & Montenegro-Johnson (2025)

$$\frac{\partial T}{\partial t} + \boldsymbol{q} \cdot \boldsymbol{\nabla} T = \frac{R}{\rho c} + \kappa \nabla^2 T + \frac{k(\phi)}{\rho c \mu_l} |\boldsymbol{\nabla} p|^2 + \frac{1}{\phi}\left(\frac{\Pi(\phi)}{\rho c} + T\right)\frac{\mathrm{d}\phi}{\mathrm{d}t}$$

External heating (1) · Thermal diffusivity (4) · Permeability · Density · Specific heat capacity · Fluid viscosity · (2) · (3) · (5)

Usually, however, reconfiguration is ‘slow’ on the timescale of heat transfer by diffusion (Lewis number – thermal diffusivity over compositional diffusivity – is large), and so we can approximate

$$\frac{\partial T}{\partial t} \approx \kappa \nabla^2 T$$

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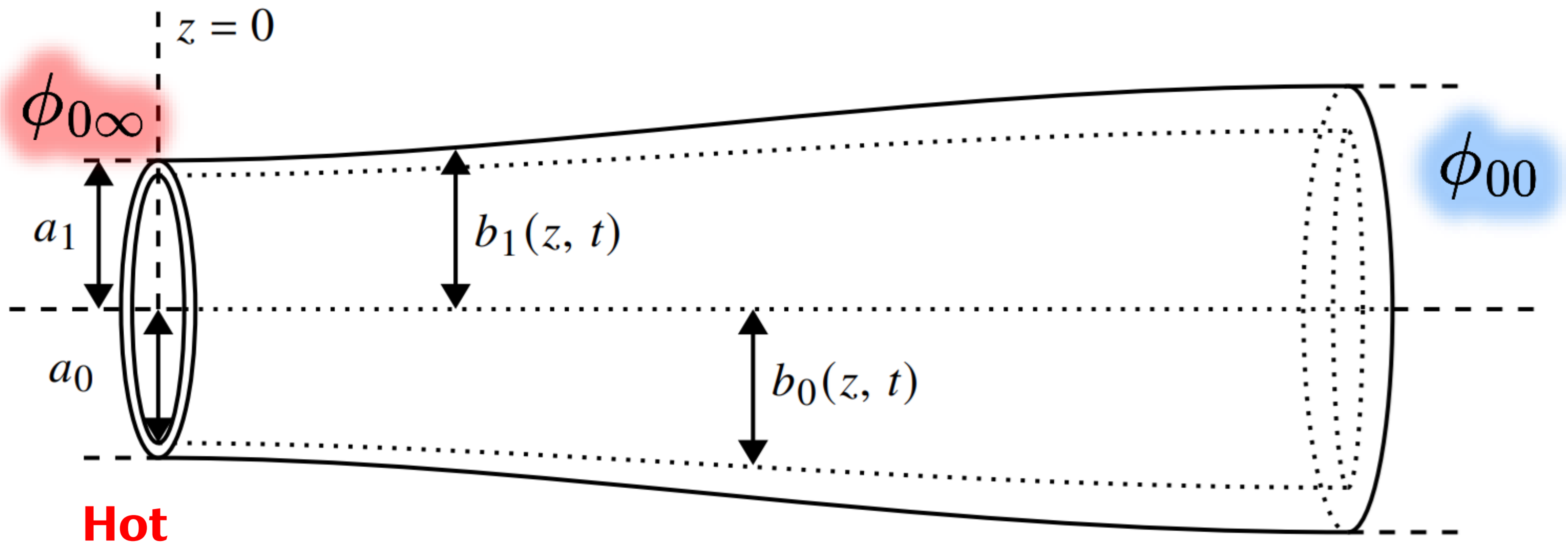
Tubes of responsive gel



Hot
Shrunken tube, narrow lumen
$T = T_C + \Delta T$

Cold $T \to T_C - \Delta T$
Relaxed tube, wide lumen

1. How does a heat pulse travel (symmetrically) outwards in time?

2. What happens to the shape of the tube as the pulse passes?

3. Where does the water go? How much is driven out radially, squeezed through the lumen, or transported along the gel?

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Heat transfer problem

1. **is easy** *(if we 'spherical cow' the problem a little…)*

The thermal diffusivity of pNIPAM gels is close to that of water, so we can treat the heat transfer problem as occurring in a single infinite domain with only variation in the *z* direction

$\kappa_{\text{gel}} \approx 1.8 \times 10^{-7}\,\text{m}^2\text{s}^{-1}$

Tél *et al.* (2014) *Int. J. Therm. Sci.* ***85:****47-53*

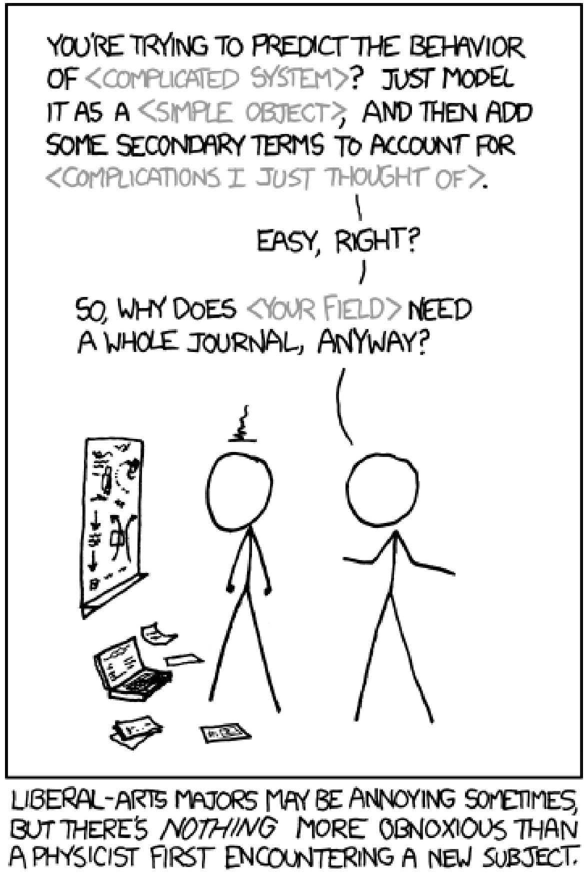
$\kappa_{\text{water}} \approx 1.43 \times 10^{-7}\,\text{m}^2\text{s}$

at 1atm and 298 K

$$T - T_C = \Delta T \left[2\,\text{erfc}\left(\frac{z}{2\sqrt{\kappa t}} \right) - 1 \right]$$

so there is a 'front' at $Z_C = 2\,\text{erfc}^{-1}\left(\frac{1}{2}\right)\sqrt{\kappa t}$ behind which the gel is deswollen

Randall Munroe *xkcd* ***793***



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Deformation of the tube

$$\frac{\partial\phi}{\partial t} + \boldsymbol{q}\cdot\nabla\phi = \frac{1}{r}\frac{\partial}{\partial r}\left[rD(\phi,T)\frac{\partial\phi}{\partial r}\right] + \frac{\partial}{\partial z}\left[D(\phi,T)\frac{\partial\phi}{\partial z}\right] \quad \text{with}$$

$$D(\phi,T) = \frac{k}{\mu_l}\left[\frac{\Pi_0(T)\phi}{\phi_0(T)} + \frac{4\mu_s}{3}\left(\frac{\phi}{\phi_{00}}\right)^{1/3}\right].$$

$\phi = \phi_0(T)$ on boundaries

slenderness assumption: aspect ratio small

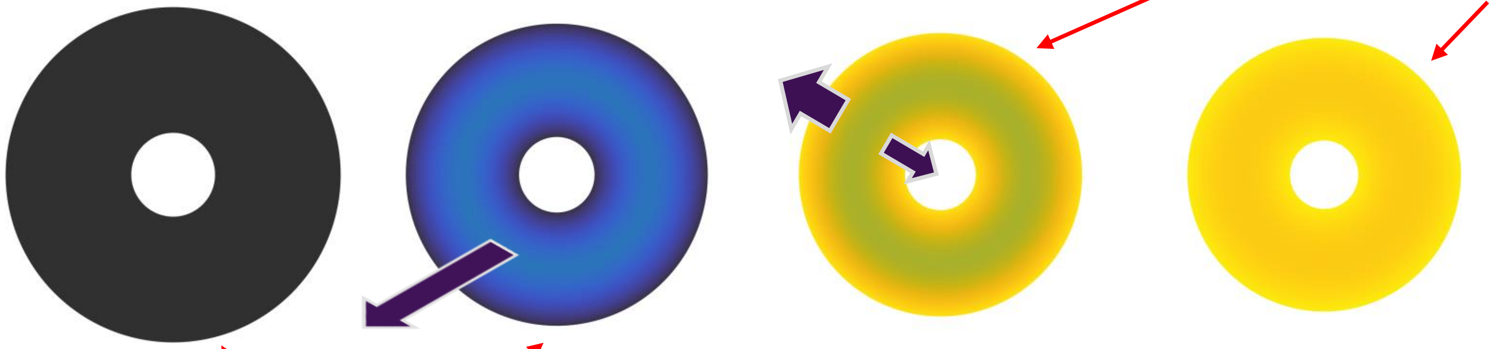
$$\phi = \phi_1(z,\, t) + \varepsilon^2\phi_2(r;\, z,\, t)$$

then separate variables

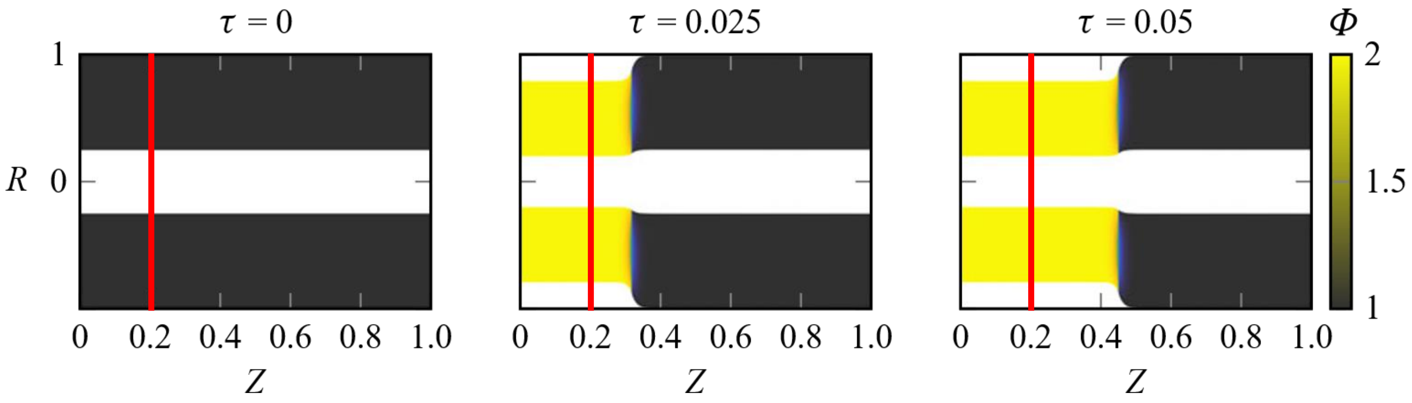
2. Shape change: is a bit harder

To attack this problem, we assume that the tube is long and thin. Balance stresses on its interface with water to find that the gel deswells to its equilibrium value on these surfaces

Fully-deswollen (inside and out)



Fully-swollen (pulse has not yet passed)



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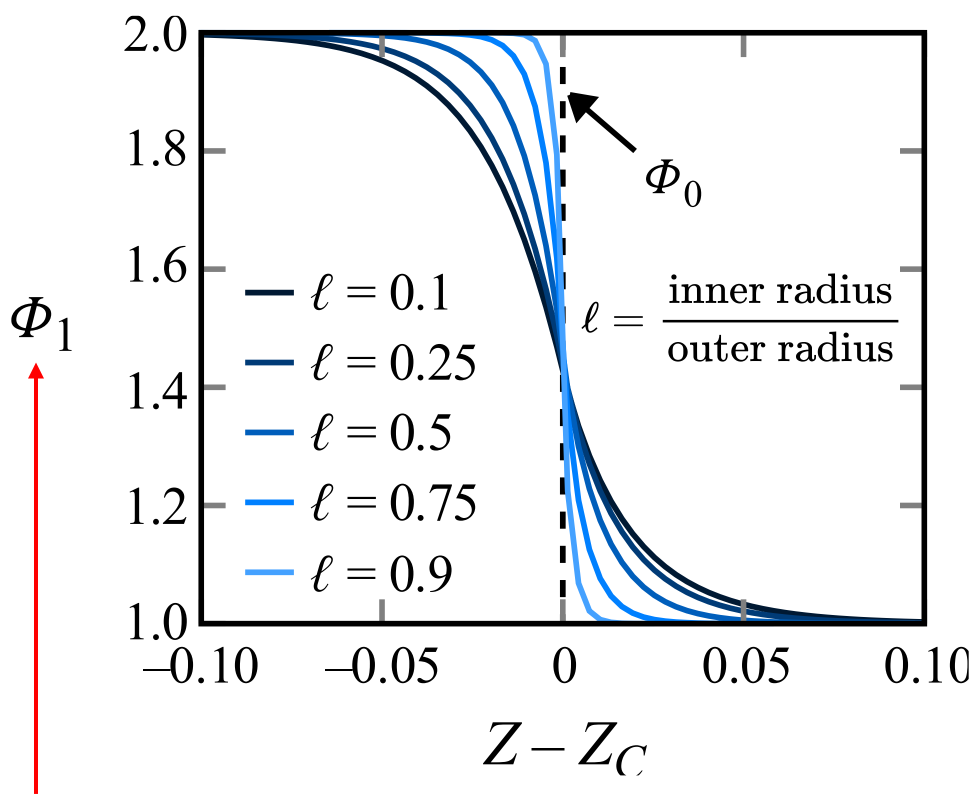
Deformation of the tube

The inside and the outside instantaneously deswell, but the interior takes some time – it's slower for a thicker tube. This leads to 'smoother' profiles for thick tubes.

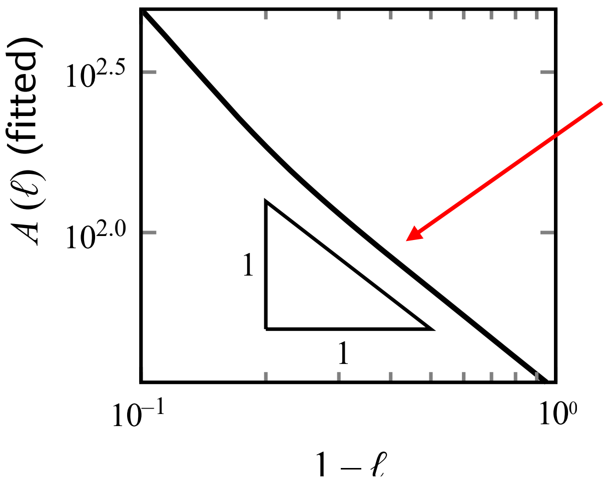


Interior (middle of tube wall) polymer fraction (scaled)

The 'smoothed step' profile suggests that we can nicely approximate the tube with a hyperbolic tangent,

$$\Phi_1 \approx \Phi_\infty - \frac{\Phi_\infty - 1}{2}\{1 + \tanh[A(\ell)(Z - Z_C)]\}$$

Dry polymer fraction (scaled)



'sharpness' of front scales like 1-ℓ

This has the corollary of quantifying how much faster the response time is for thinner walls

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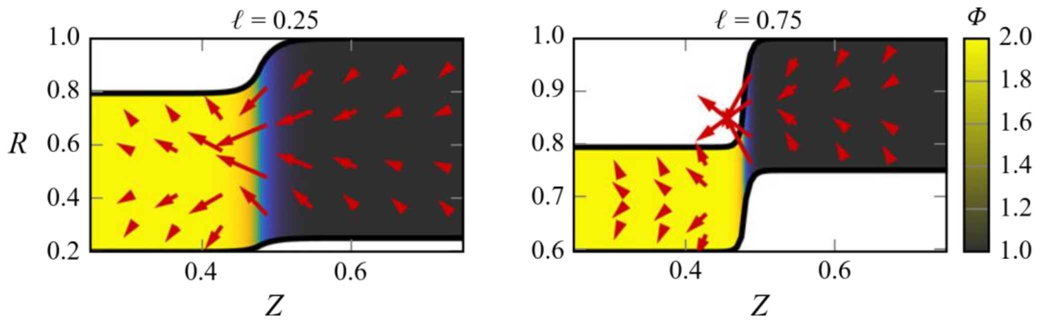
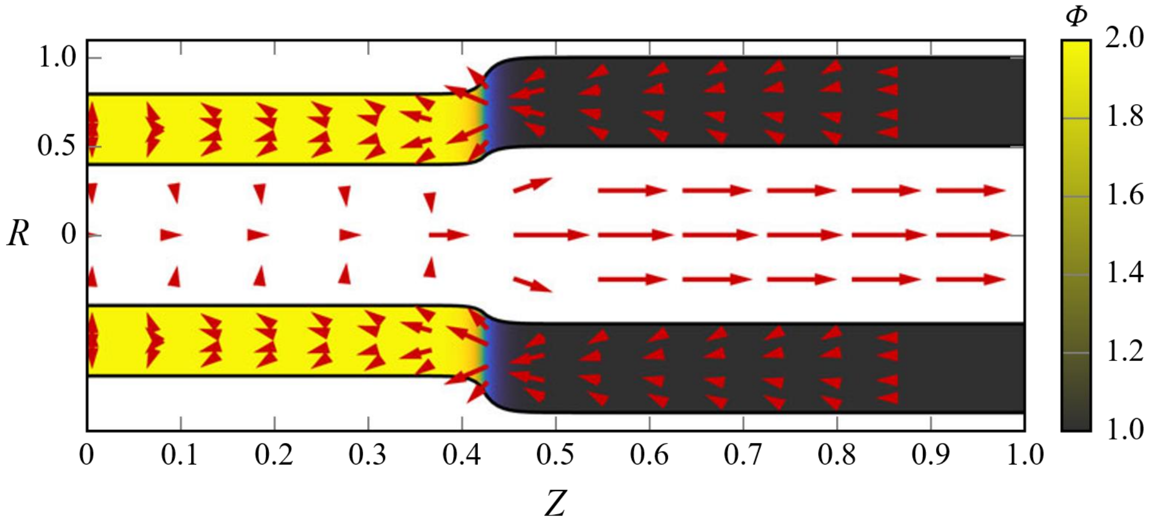
The fluid pulse

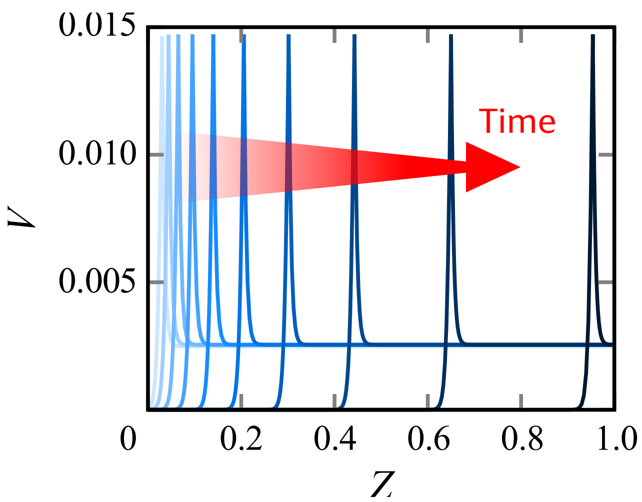


3. Fluid flows

Flows arise in three places:

- Radial fluxes from the tube walls into the surroundings as they deswell – $u_r \propto \partial\phi/\partial r$
- Axial fluxes through the gel from more swollen to less swollen regions (probably small) – $u_z \propto \partial\phi/\partial z$
- Axial fluxes arising from conservation of fluid: the tube collapses and squeezes water along its length





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UK Hydrogels seminars


PROCEEDINGS A

Cryosuction and freezing hydrogels

Joseph J. Webber and M. Grae Worster

1. Introduction

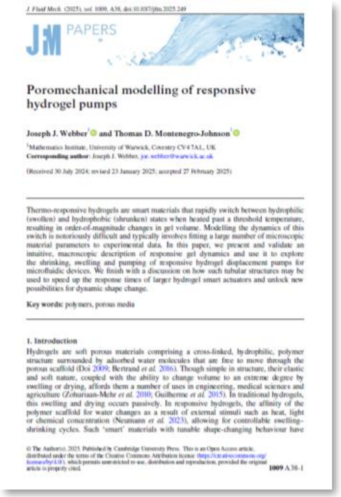
THE ROYAL SOCIETY PUBLISHING

Cryosuction and freezing hydrogels

JJW & M. Grae Worster (2025)

Proc. Roy. Soc. A **481:**20240721

doi:10.1098/rspa.2024.0721


JFM PAPERS

Poromechanical modelling of responsive hydrogel pumps

Joseph J. Webber and Thomas D. Montenegro-Johnson

Key words: polymers, porous media

1. Introduction

Poromechanical modelling of responsive hydrogel pumps

JJW & Thomas D. Montenegro-Johnson (2025)

J. Fluid Mech. **1009:**A38

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