Royal Society Publishing Fluid Mechanics Seminars
Wednesday 18th June 2025

Freezing of hydrogels

modelling cryosuction, deformation and ice growth

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based on **Webber & Worster** 'Cryosuction and freezing hydrogels' Proc. Roy. Soc. A 481 (2025)

Freezing soft watery materials

We all see examples of how soft, porous, water-filled materials get damaged when they freeze:

- **Thermal expansion?** ice has a volume ~9% greater than that of liquid water
- **Freeze-thaw weathering?** repeated expansion and contraction = damage
- **Microscale damage?** cells burst when frozen and their membranes are permanently destroyed

$(L/L_0)^3 = V/V_0 \approx 1.09$ hence $\epsilon = (L - L_0)/L_0 \approx 0.02$ and stresses scale like $0.02E$

Fracture occurs when the stresses are larger than the strength, so need *strength/elastic modulus* to be greater than ~1/50


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Material	Elastic modulus (Pa)	Yield strength (Pa)
strawberry *An et al. 2023*	10^5	2×10^4
pNIPAM *Xia et al. 2013*	~ 5×10^4	~ 5×10^4

Freezing soft watery materials

We all see examples of how soft, porous, water-filled materials get damaged when they freeze:

- Thermal expansion? ice h... water
- Freeze-thaw weathering... age
- Microscale damage? cell... e permanently destroyed

$(L/L_0)^3 = V/V_0 \approx 1.09$ hence ... ke $0.02E$

Fracture occurs when the stresses ... *modulus* to be greater than ~1/50

Why hydrogels?

Soft: low elastic modulus
Can be brittle: break with small(ish) strain
Clear: we can see what's going on inside
Highly porous: large water content

Ignore applications for now – we will only consider gels as a model material

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Ice formation in gels and cryosuction

1. Ice doesn't form in the pore spaces (mostly)

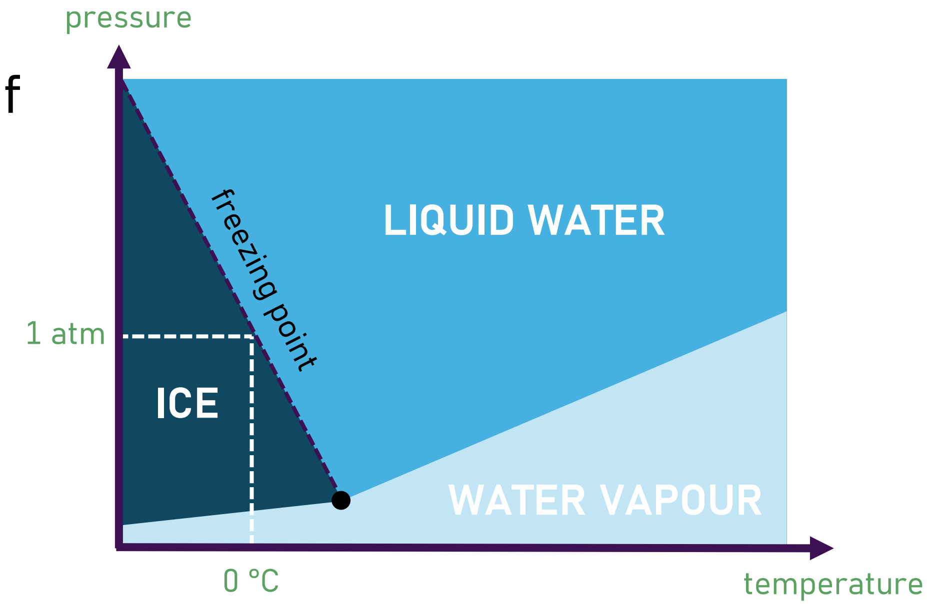
The pressure, owing to capillarity, inside the nanoscale pores of a hydrogel depresses the freezing temperature, so ice forms segregated from the porous medium.

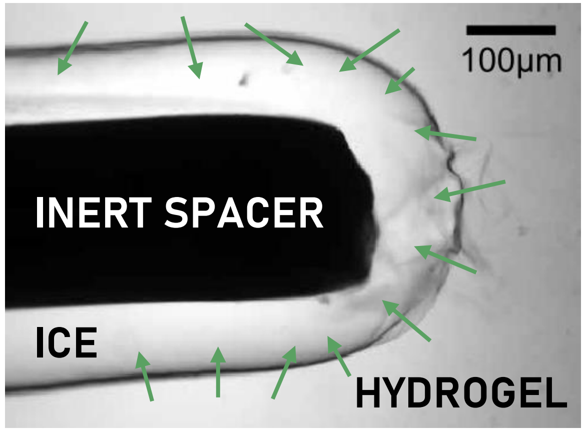
$$T_{IE} = T_m \left[1 - \frac{\gamma\kappa}{\rho_{\text{ice}}\mathcal{L}}\right]$$

surface tension and average pore curvature

equilibrium freezing temperature (~273 K)

specific latent heat of fusion





Yang *et al.* Sci. Adv. 10:eado7750 (2024)

2. Ice grows by cryosuction

Water is drawn out of the gel to grow ice – **this resolves the apparent thermal expansion paradox** and leads to large strains. The volume of an 'ice lens' can be significantly larger than the space previously occupied by water.

The Clausius-Clapeyron relation

Stress in the ice and/or the gel modifies the melting point: large stresses depress the freezing temperature

normal stress in the gel

liquidus temperature

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

specific latent heat of fusion

In a hydrogel, the stress tensor can be decomposed into an isotropic pressure and a deviatoric stress. This pressure has two parts:

- **Pore (pervadic) pressure *p*:** this is the pressure of the liquid component, and gradients in *p* drive flows. Furthermore, this is continuous at an ice-gel boundary so $p_{gel} = p_{atm}$ here.
- **Generalised osmotic pressure *Π*:** this arises from isotropic elasticity *and* osmotic effects and is just a function of the swelling state

polymer volume fraction

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

deviatoric strain

shear modulus

The Clausius-Clapeyron relation

normal stress in the gel

liquidus temperature

specific latent heat of fusion

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

Using the fact that the normal stress must balance pressure in the ice (continuity of stress)

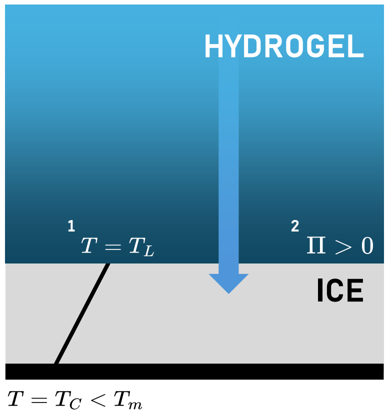
$\boldsymbol{n}\cdot\boldsymbol{\sigma}\cdot\boldsymbol{n} + p_{\mathrm{atm}} = 0$ and $p_{\mathrm{gel}} - p_{\mathrm{atm}} = -\left[\boldsymbol{n}\cdot\boldsymbol{\sigma}\cdot\boldsymbol{n} - \Pi(\phi)\right] - p_{\mathrm{atm}} = \Pi(\phi)$

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

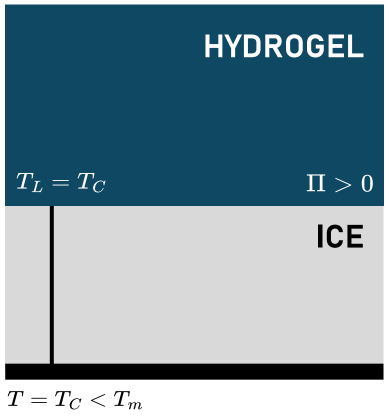
1. As a BC on temperature
sets a lower temperature at a dried gel interface

2. As a BC on gel
sets a higher polymer fraction at a colder interface

ice forms at the cold boundary



ice grows and the gel dries to form it



a steady state is reached

Modelling one-dimensional freezing

The thermal problem

$$\frac{\partial T}{\partial t} = \kappa \frac{\partial^2 T}{\partial z^2} \quad \begin{cases} \text{in the ice } 0 < z < a(t) \\ \text{in the gel } a(t) < z < h \end{cases}$$

$T = T_C$ at $z = 0$

$\partial T/\partial z = 0$ at $z = h$

whilst at the interface *z* = *a(t)*,

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

$$\rho_{\text{ice}}\mathcal{L}\frac{\mathrm{d}a}{\mathrm{d}t} = -\left[\mathcal{K}\frac{\partial T}{\partial z}\right]_-^+$$

Growth rate of ice is governed by an energy balance (Stefan condition) – latent heat matches the difference in fluxes across the boundary

The gel problem

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

To describe the response of a gel, there are three material parameters:

$\Pi(\phi)$	$\mu_s(\phi)$	$k(\phi)$
osmotic pressure	shear modulus	permeability

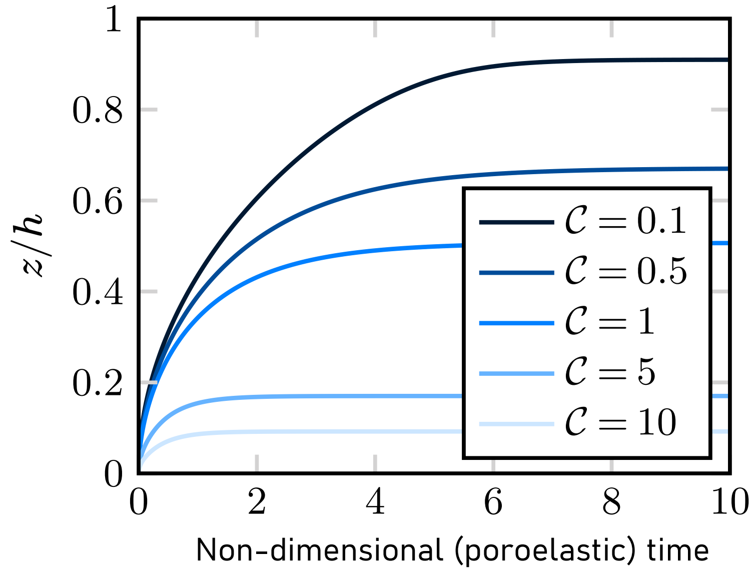
$$\frac{\partial \phi}{\partial t} = \frac{\partial}{\partial z}\left[D(\phi)\frac{\partial \phi}{\partial z}\right] \qquad \frac{\partial \phi}{\partial z} = 0 \qquad \Pi(\phi) = \rho_{\text{water}}\mathcal{L}(T_m - T_L)$$

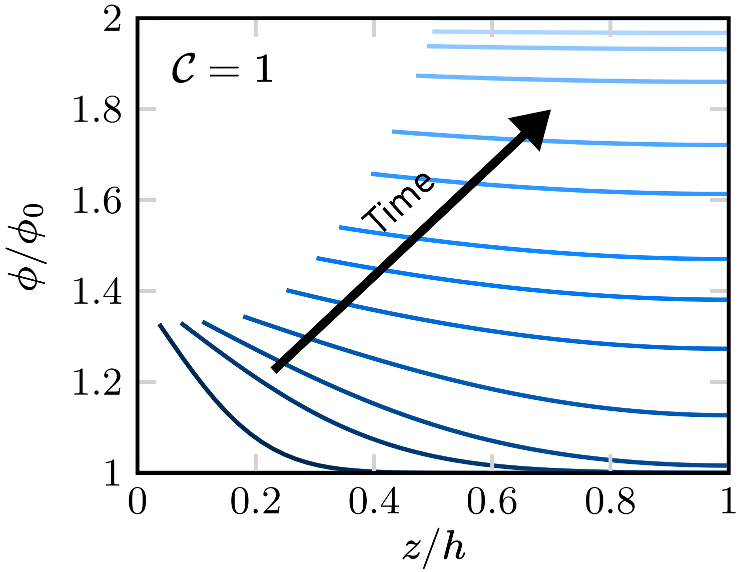
in the gel $a(t) < z < h$ — at $z = h$ — at $z = a(t)$

Growth rate of ice governed by mass balance at the interface,

$$\frac{\mathrm{d}a}{\mathrm{d}t} = -\frac{D(\phi)}{\phi}\frac{\partial \phi}{\partial z}$$

Modelling one-dimensional freezing





The extent of freezing is set by a non-dimensional undercooling parameter $\mathcal{C}$

$\Pi = \Pi_0(\phi - \phi_0)/\phi_0$

$$\mathcal{C} = \frac{\Pi_0 T_m}{\rho_{\text{ice}}(T_m - T_C)}$$

Ice forms by drawing water down from initially-swollen gel, drying it at the ice-gel interface, until a steady state is reached where osmotic pressures lower the freezing temperature to the cold boundary temperature T_C

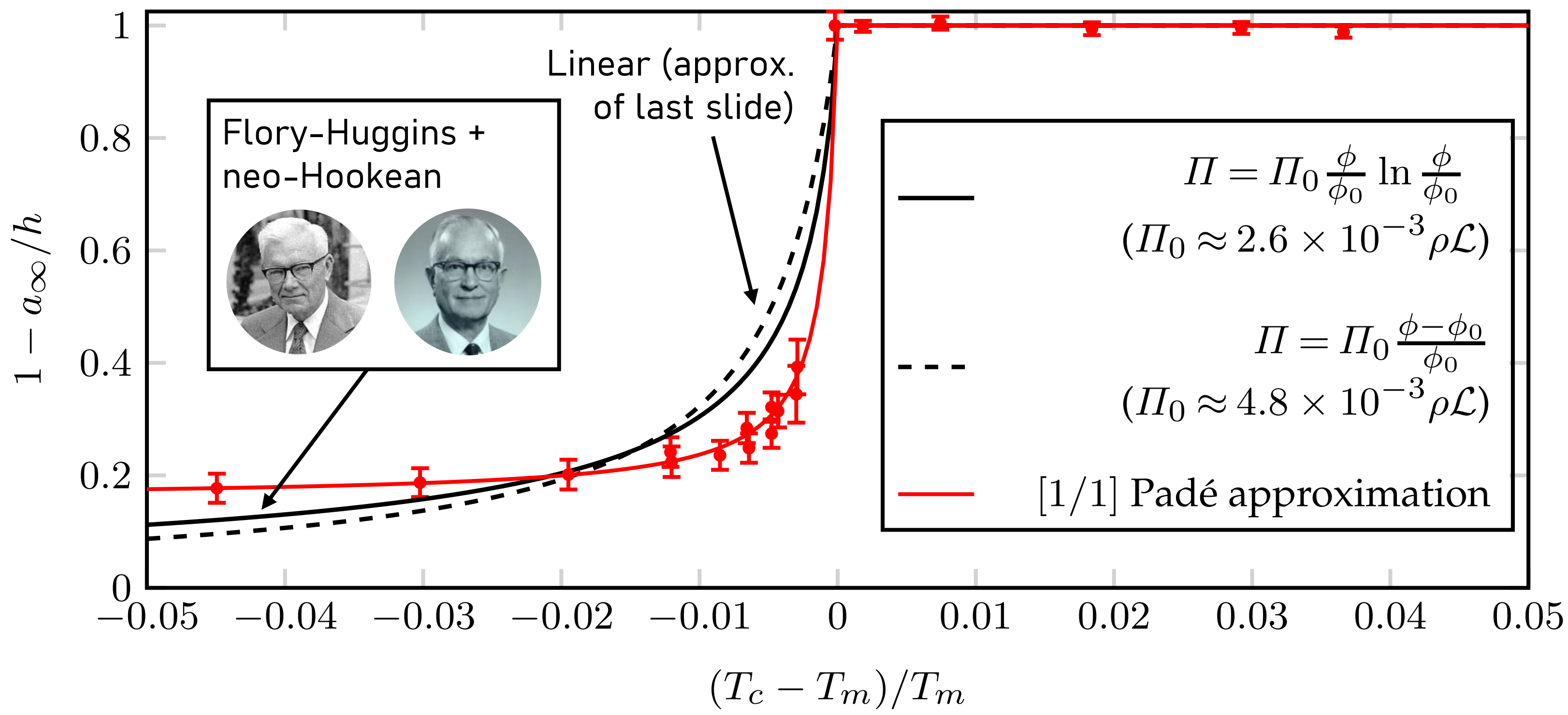
So, in steady state, irrespective of the form of Π

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

Gel-freezing osmometry (GelFrO)

This steady-state balance is the basis for gel-freezing osmometry, a new technique recently introduced by **Feng et al.** (2025) *J. Mech. Phys. Solids* ***201:****106166*

Freezing allows us to probe the microscopic properties of a hydrogel using only macroscopic measurements!

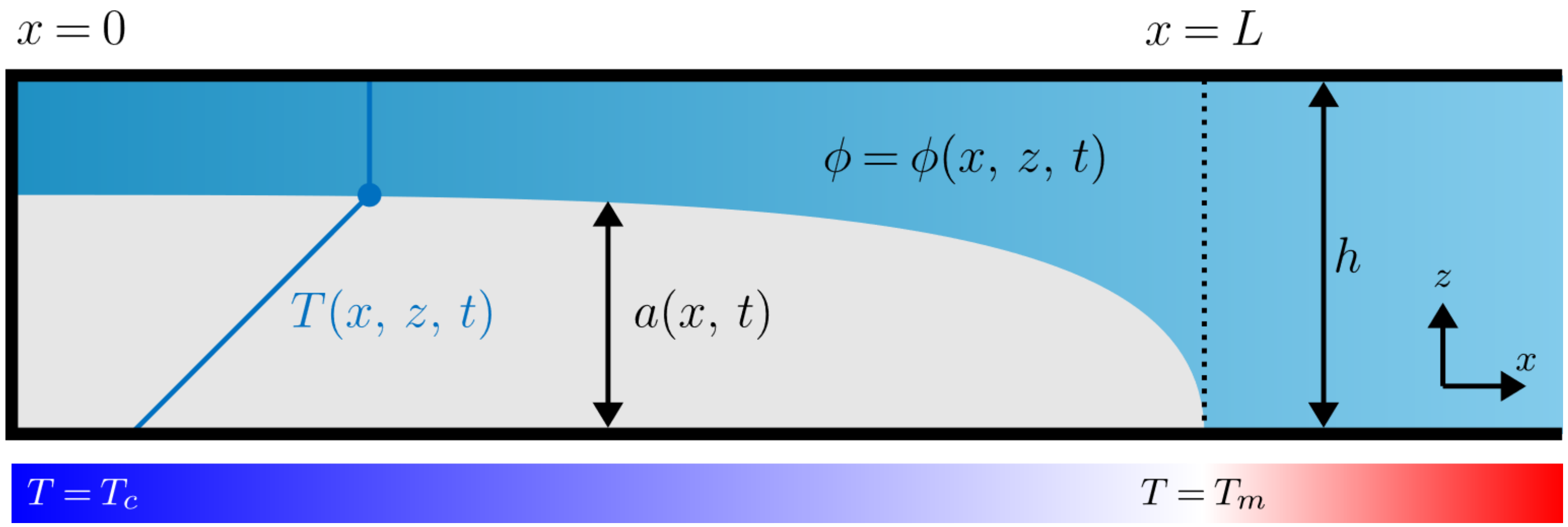


$$\Pi\left(\frac{\phi_0 h}{h - a_\infty}\right) = \rho_{\text{water}} \mathcal{L} (T_m - T_C)$$

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

Forming ice 'lenses'

Freezing leads to stress buildup in the dried gel that remains; in our 1D example, this stress is uniform (eventually) through the gel. In 2D, however, the picture is more complicated



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

$$T = T_m \ (x \geq L)$$

chosen to give continuity and a continuous first derivative at $x = L$

Forming ice 'lenses'

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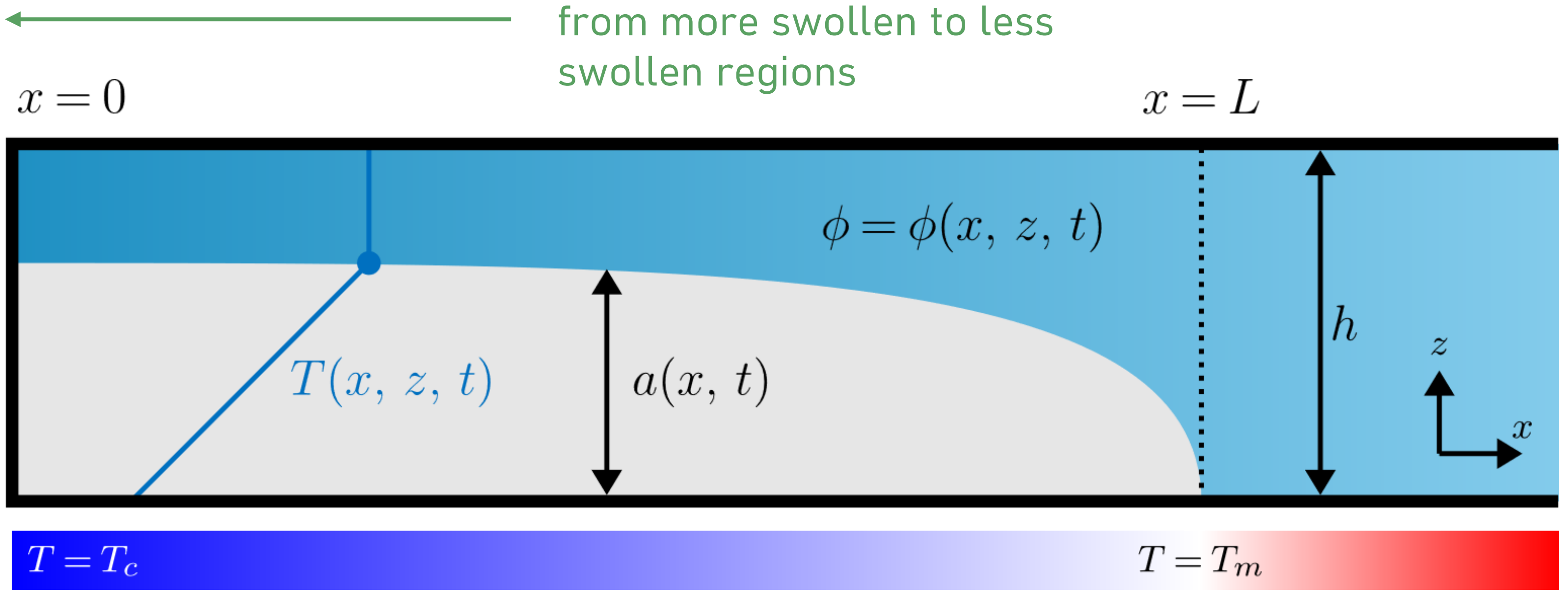
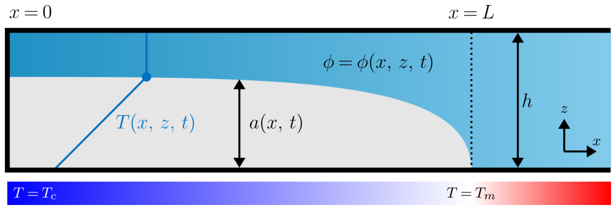


This feedback cycle only breaks when reswelling can't occur any longer. What's missing?

drying (↖) → osmotic stress (↖) → pore pressure (↗) → flow (←)

OR drying (↖) → elastic stress (↖) → pore pressure (↘) → flow (→) ?

Pervadic pressure in the deformed gel



Returning to the momentum balance,

$$\nabla p + \nabla \Pi = 2\nabla \cdot [\mu_s(\phi)\boldsymbol{\epsilon}]$$

need to know the displacement of the hydrogel to determine this!

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

To solve this analytically, introduce a small parameter $\varepsilon = h/L$ and use a linear osmotic pressure and constant shear modulus

$$\nabla \cdot \boldsymbol{\epsilon} = \nabla \cdot \mathbf{e} - \frac{1}{2}\nabla\,(\mathrm{tr}\,\mathbf{e}) = \frac{1}{2}\nabla^2\boldsymbol{\xi} + \frac{1}{2}\nabla(\nabla \cdot \boldsymbol{\xi}) - \frac{1}{2}\nabla(\nabla \cdot \boldsymbol{\xi}) \quad \text{so} \quad \mu_s\nabla^2\boldsymbol{\xi} = \Pi_0\nabla\left(\frac{\phi}{\phi_0}\right) + \nabla p$$

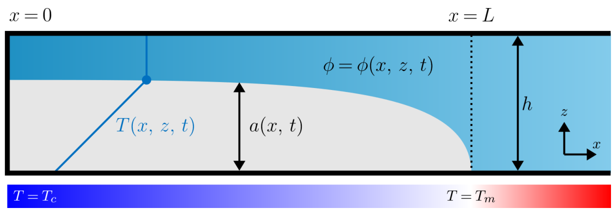
Displacement from swollen equilibrium $\boldsymbol{\xi} = (\xi, \eta)$

$$\xi \approx \frac{z^2}{2\mu_s}\frac{\partial}{\partial x}(p + \Pi) + A(x)z + B(x) \quad \text{and use} \quad \nabla \cdot \boldsymbol{\xi} = 2\left[1 - (\phi/\phi_0)^{1/2}\right] \quad \text{to find } \eta$$

momentum balance → displacement field in terms of p and ϕ

Gel modelling and BCs on displacement give ϕ, p

Dynamics of ice lens growth



The thermal problem

- Linear profile in the ice, equal to liquidus on boundary, constant (at liquidus) in gel.

  ***Why?** Thermal diffusion much faster than poroelastic reconfiguration, so assume quasi-steady temperature field.*

- Ice growth again from Stefan condition

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

undercooling at boundary — osmotic slowdown

The gel problem

Making slenderness approximations, we find

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

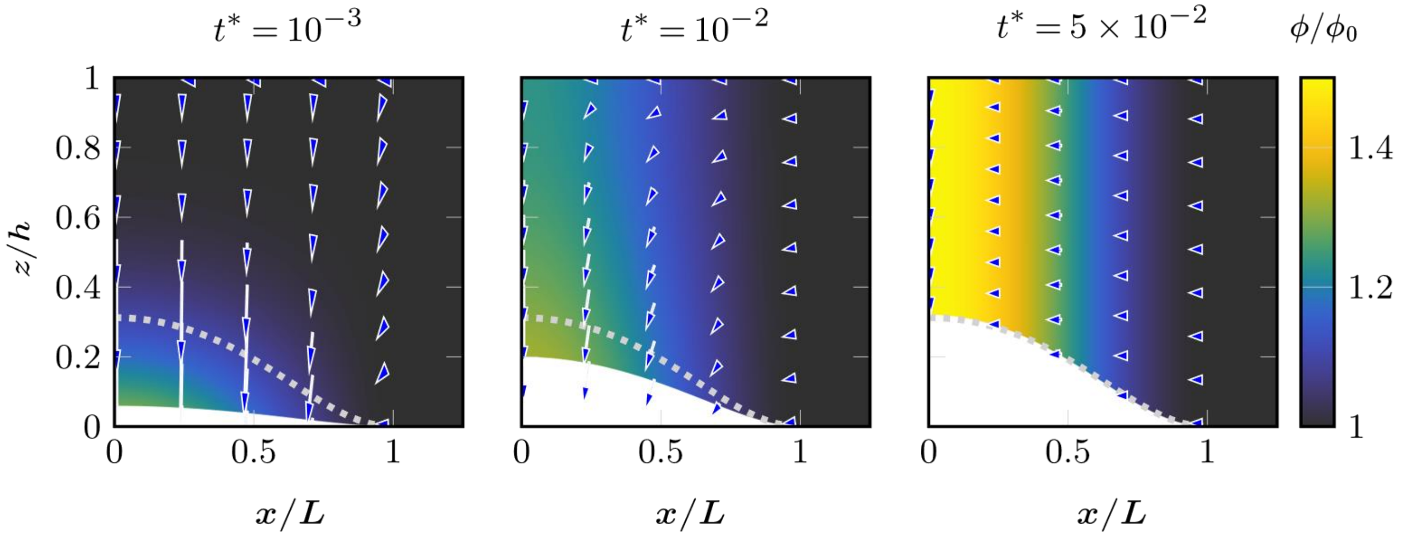
- Polymer fraction set by liquidus relation on boundary
- Neumann BCs on walls (no flow)

Boundary conditions on walls depend on how sticky the boundaries are!

- **No-slip (adhered)** implies $\xi = 0$ on $z = a(x, t), h$
- **Free-slip** implies $\partial\xi/\partial x = 0$ on $z = a(x, t), h$

In either case, $\eta = 0$ on $z = h$ and $\eta = a(x, t)$ on $z = a(x, t)$

Dynamics of ice lens growth



Solving the system detailed on the previous slide reproduces the dynamics we predicted at the outset

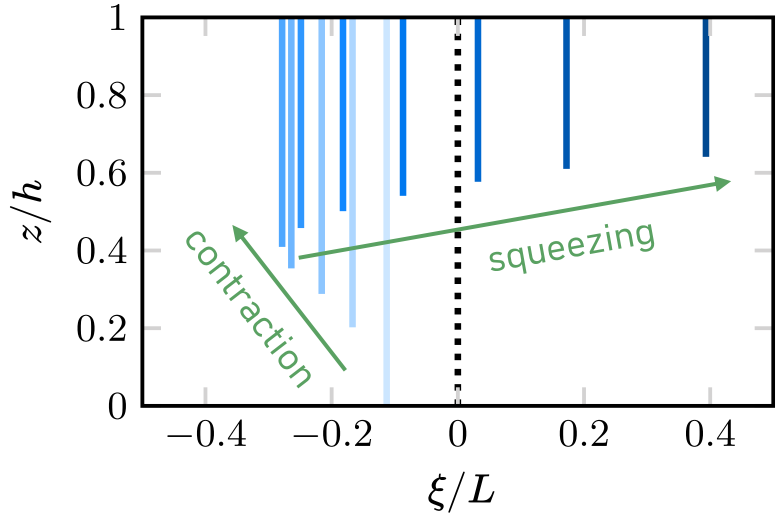
time scaled on poroelastic timescale, free-slip BCs
interstitial fluid velocity shown as blue arrows

Plotting the displacement shows two key regimes:

Contraction when the gel deswells, driving fluid to the ice and shrinking back in response

$$a \approx \sqrt{\frac{\mathcal{K}}{\rho \mathcal{L}}(T_m - T_C)\left(1 + \cos\frac{\pi x}{L}\right) t}$$

Squeezing when the growing ice compresses the gel and 'extrudes' it horizontally to the right

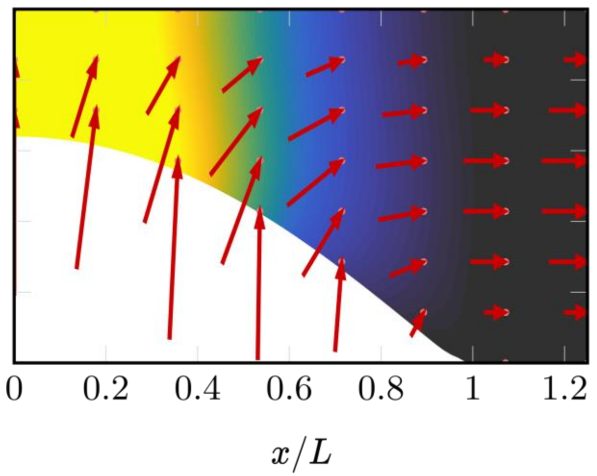


The displacement field

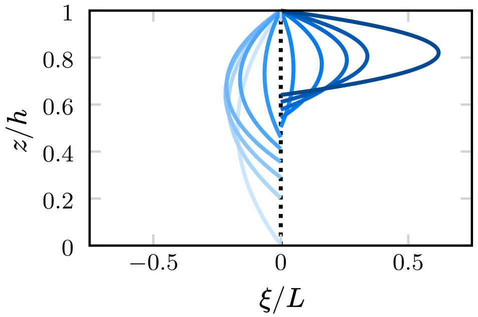
No-slip boundary conditions

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

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



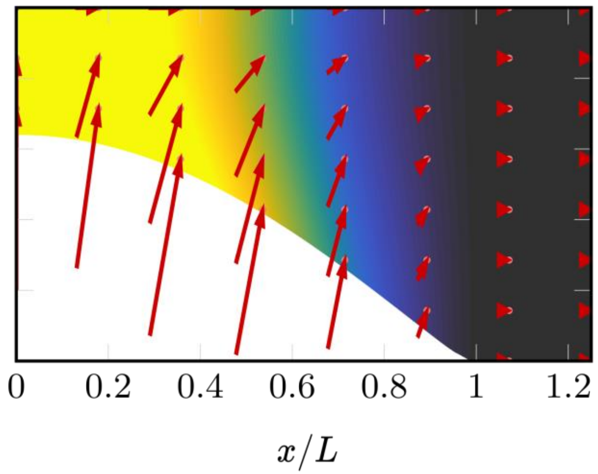
requires large stiffness



Free-slip boundary conditions

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

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



requires little drying;
no dependence on elasticity

The steady state

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

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

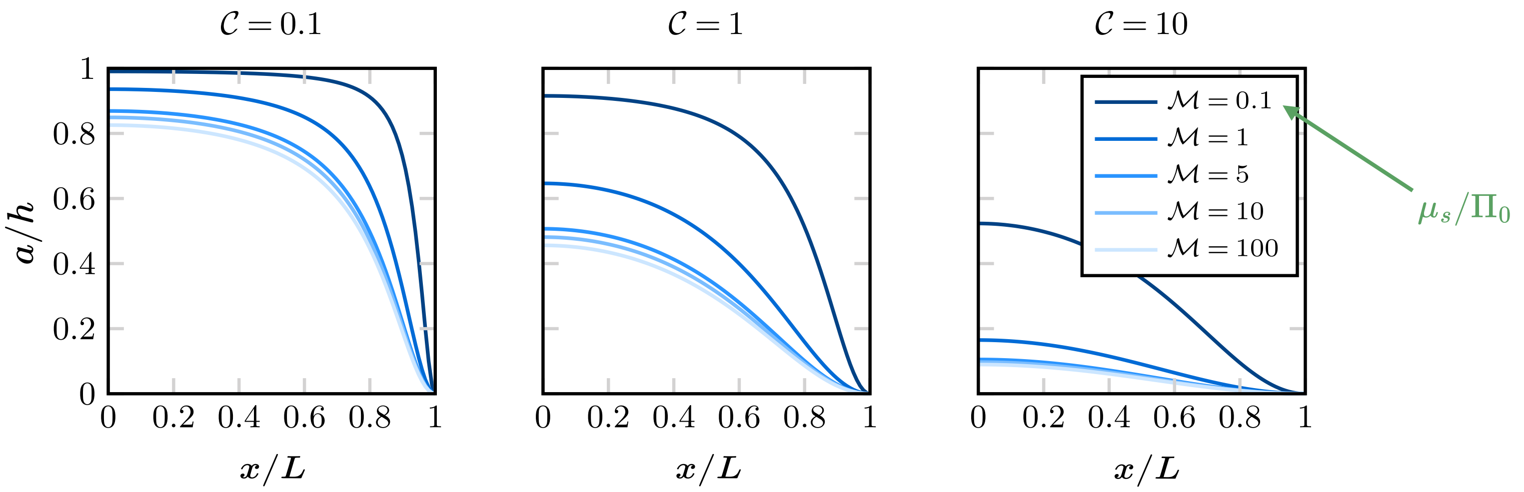
gel sits on liquidus

slenderness approximation

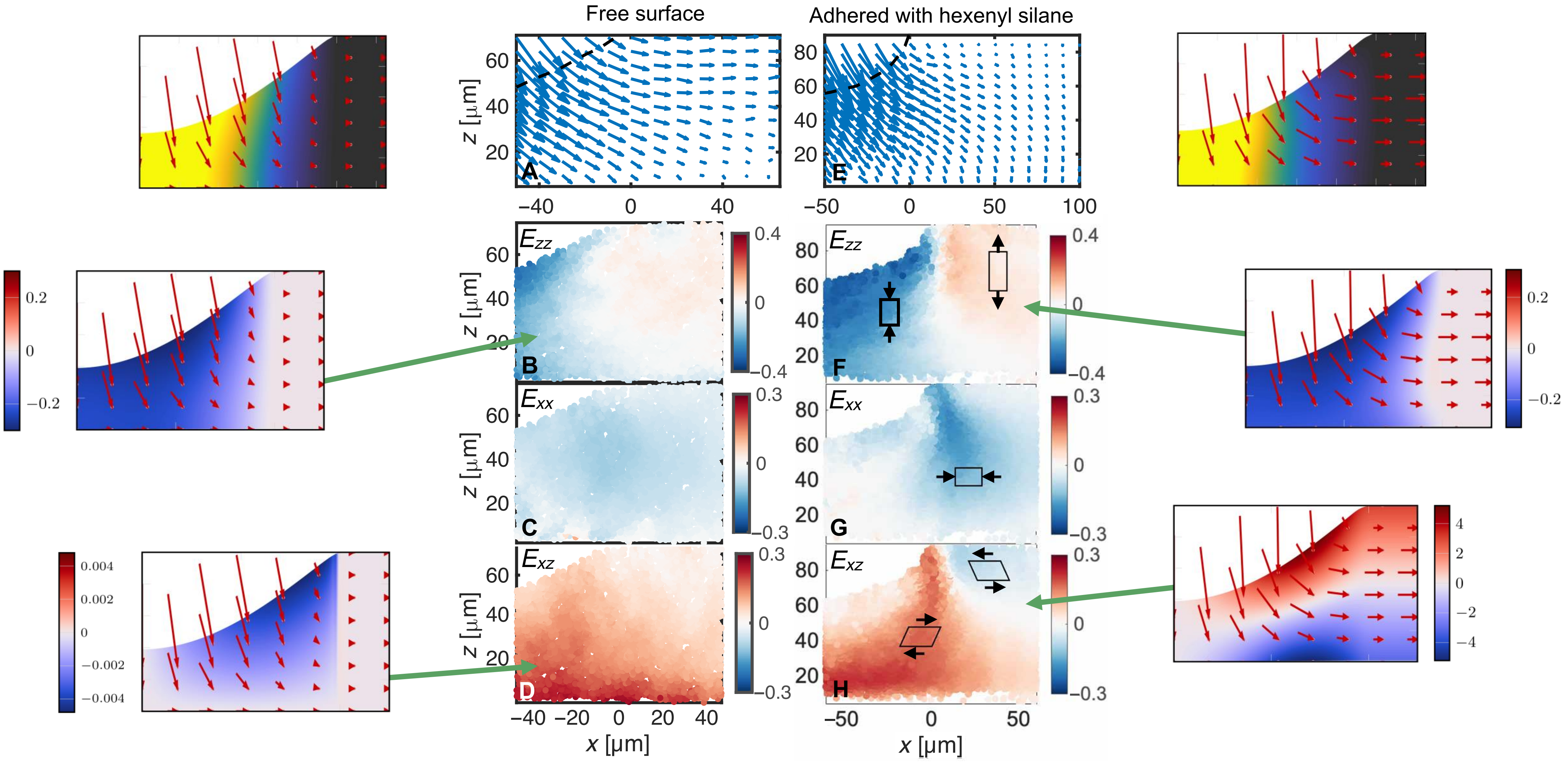
giving $\phi = \phi_\infty(x)$ with $\Pi(\phi_\infty) = \dfrac{\rho \mathcal{L}}{2}\left(1 - \dfrac{T_C}{T_m}\right)\left(1 + \cos\dfrac{\pi x}{L}\right)$

Need deviatoric stresses to balance these osmotic pressures exactly or else there is flow.

$$\mathcal{C} = \frac{\Pi_0 T_m}{\rho_{\text{ice}}(T_m - T_C)}$$



Stresses and strains



MODE I

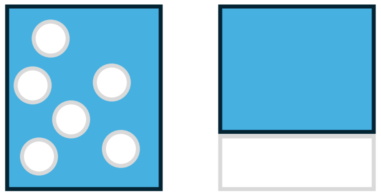
MODE II

central figure from Yang *et al.* Sci. Adv. 10:eado7750 (2024)

Understanding and controlling damage

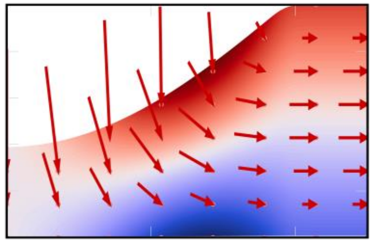
How can we minimise damage, then, to soft materials when freezing them?

- **Changing the temperature:** dependent on whether we want to freeze water *in situ* (and thus only worry about thermal expansion) or preserve cell structures, we can choose a temperature either side of the ice-entry value



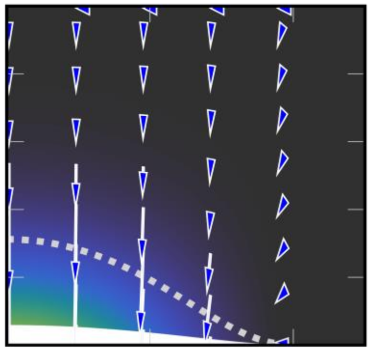
- **Change the confinement:** materials bound to stiff substrates build up more damage as deviatoric strains can be significant.

  This is key in transplant organs, which should perhaps be detached from stiffer materials such as tendons to preserve them better



- **Change the rate:** suction can cause damage, and our model quantifies the interstitial flow velocities as a function of undercooling

$$a \approx \sqrt{\frac{\mathcal{K}}{\rho \mathcal{L}} (T_m - T_C) \left(1 + \cos \frac{\pi x}{L}\right) t}$$



Summary

- **Ice can't form in the pores of gels:** it instead forms at a boundary and water is sucked through the porous scaffold to grow more and more of it.
  - This is the key driver of damage as ice can grow by more than just thermal expansion

- **Drying a gel depresses the freezing temperature:** as osmotic pressures change the liquidus relation.
  - Freezing can therefore be used to probe the osmotic pressure of a hydrogel (Feng *et al.*, 2025)

- **In 2D and 3D, (shear) elasticity comes in to play:** steady states are set by a balance of elastic, osmotic and thermal effects.
  - Displacement boundary conditions are key to the dynamics of freezing and the growth of stresses
  - The mode of damage to a soft material depends strongly on what happens at the boundaries (Yang *et al.*, 2024)

Royal Society Publishing Fluid Mechanics Seminars
Wednesday 18th June 2025

more details can be found in

Webber, J. J. & Worster, M. G.
Cryosuction and freezing hydrogels
Proc. Roy. Soc. A 481 (2025)

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