MS27: Prize winners from the 2025 IMA Lighthill Thwaites Prize
BMC-BAMC Exeter, Wednesday 25th June 2025, 17:20

Getting stressed about frozen gels

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

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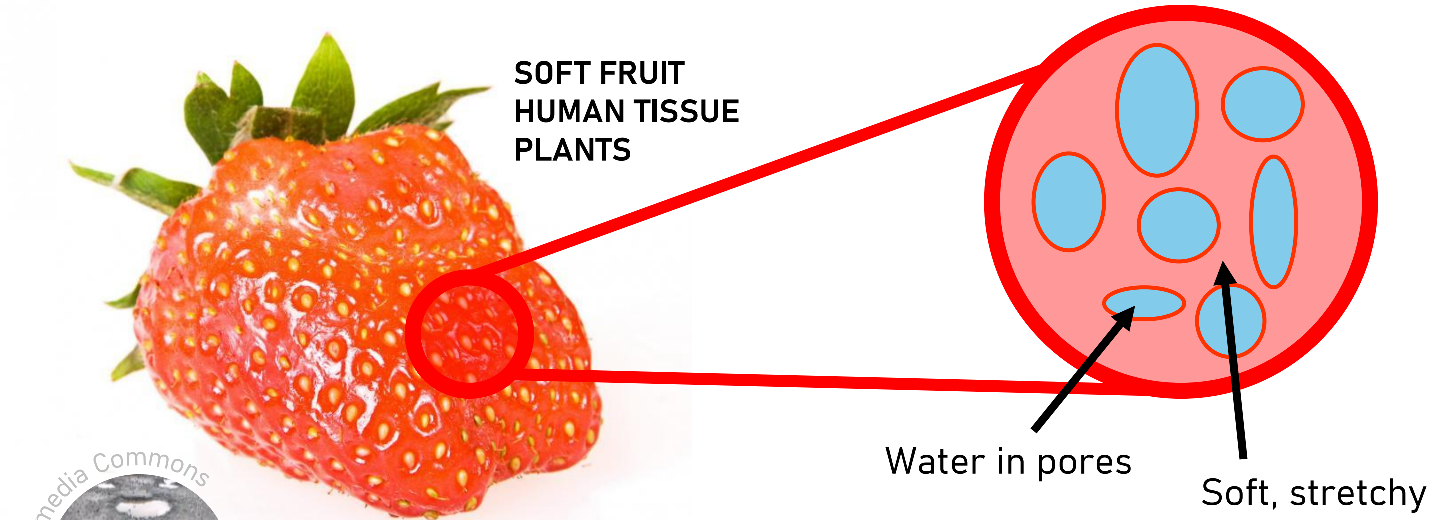
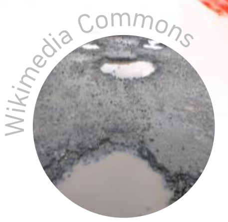
How do deformable porous media freeze?





TARMAC

SOIL

$$(L/L_0)^3 = V/V_0 \approx 1.09$$

$$\epsilon = (L - L_0)/L_0 \approx 0.02$$

stresses must therefore scale like *0.02E*

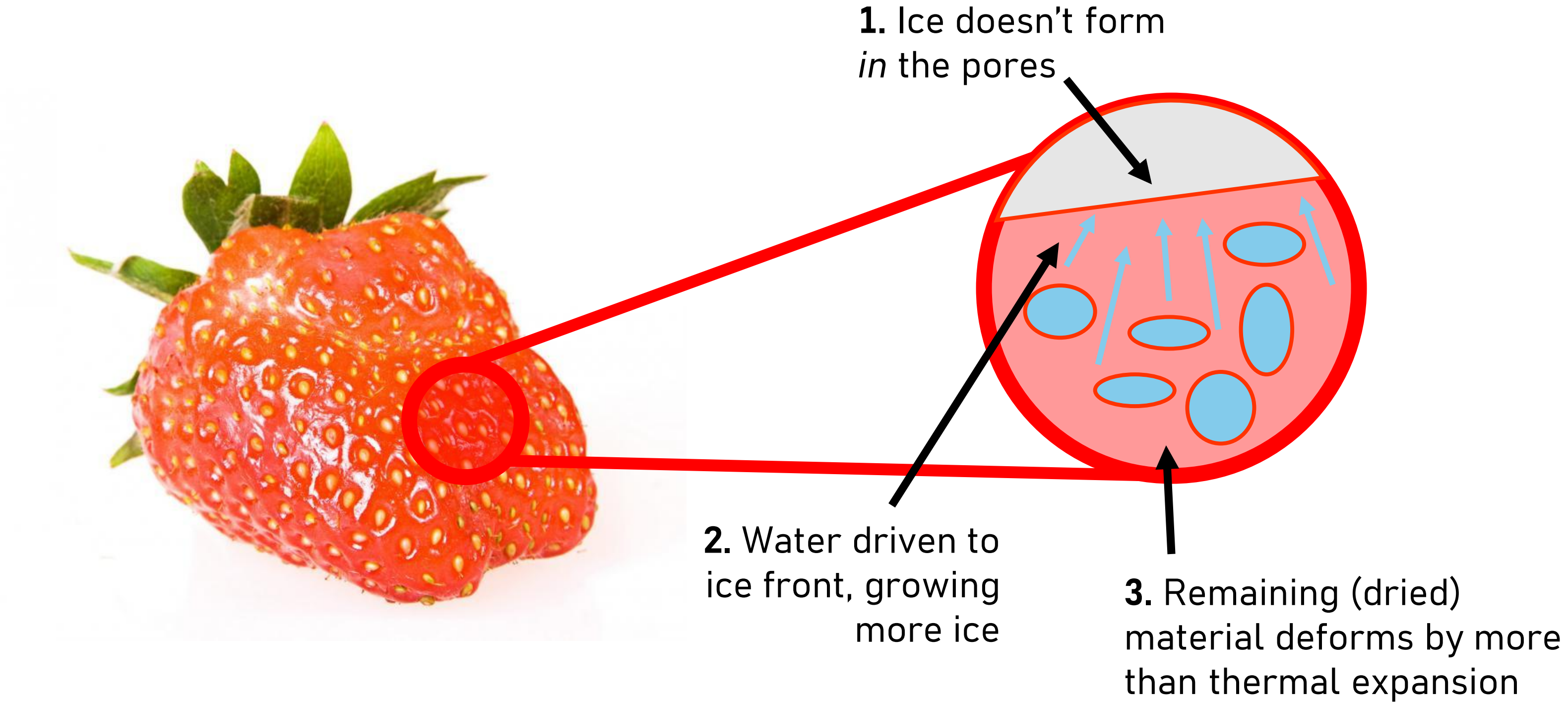
but, for a strawberry, *E* ~ 10^5 Pa yet the fracture strength ~ 2×10^4 Pa

An *et al.* Food Res. Int. **169:**112787 (2023)

Why does freezing cause damage?

- ~~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

Cryosuction



Freezing temperature lowered due to capillarity in pores

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

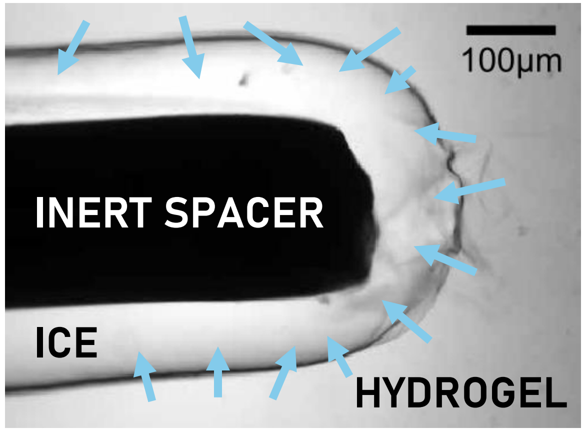
surface tension and pore curvature

equilibrium freezing temperature (~273 K)

specific latent heat of fusion

- Ice growth and material–ice boundary conditions
- Deformation of the remaining material
- Flow of water due to cryosuction

Use hydrogels as a proxy material: tuneable and can 'see inside'



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

How does ice grow from a hydrogel?

Stresses in the hydrogel modify the freezing point, but we must quantify these stresses

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

polymer volume fraction

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

shear modulus

deviatoric strain

pressure =

pervadic pressure

Peppin *et al.* Phys. Rev. E 17:053301 (2005)

≈ pore pressure, chemical potential

"the pressure of the water inside the pores"

+

isotropic elasticity + osmotic pressure

= generalised osmotic pressure *Π(ϕ)*

depends only on amount of swelling

"the pressure acting to close stretched pores"

"the pressure arising from how hydrophilic a gel is"

Freezing (liquidus) temperature given by the Clausius-Clapeyron relation

liquidus temperature

normal stress in gel

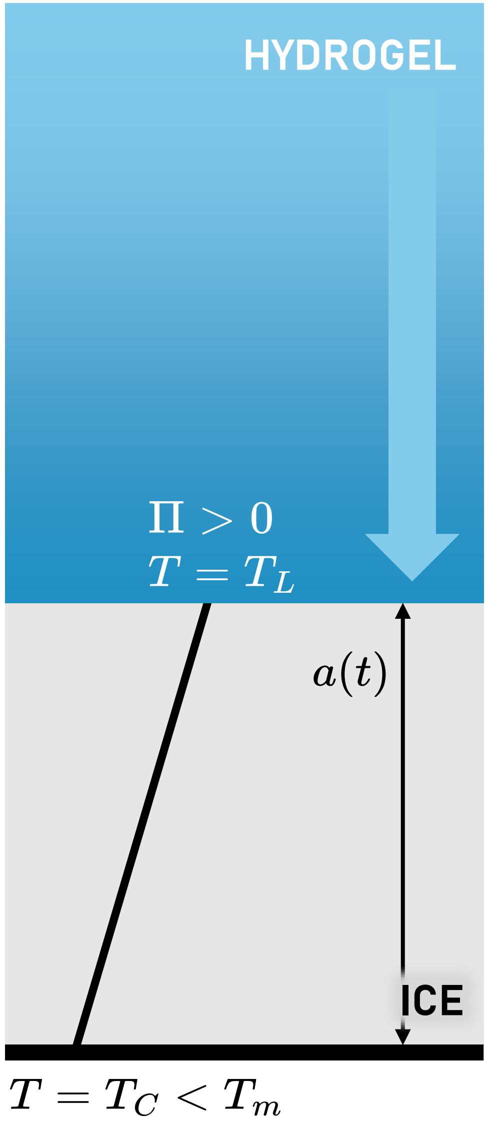
$$\mathcal{L}\frac{T_L - T_m}{T_m} = \frac{\boldsymbol{n}\cdot\boldsymbol{\sigma}\cdot\boldsymbol{n} + p_{\text{atm}}}{\rho_{\text{ice}}} + \frac{p_{\text{gel}} - p_{\text{atm}}}{\rho_{\text{water}}}$$

specific latent heat of fusion

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

"large osmotic pressure lowers the freezing temperature"

How does ice grow from a hydrogel?



Clausius-Clapeyron relation: temperature depends on how dry the gel is

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

BC on polymer fraction

Temperature sets the amount of drying

BC on temperature

How dry the gel is sets the temperature

Stefan condition: growing ice uses up energy

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

Quasi-steady thermal problem implies T is linear (in ice),

$$\frac{\mathrm{d}a}{\mathrm{d}t} = \frac{\mathcal{K}}{\rho_{\text{ice}} \mathcal{L}} \frac{(T_m - T_C) - T_m \Pi(\phi)/\rho_{\text{water}} \mathcal{L}}{a(t)}$$

Mass conservation: to form ice, water must be drawn from the hydrogel

$$\rho_{\text{ice}} \frac{\mathrm{d}a}{\mathrm{d}t} = -\rho_{\text{water}} \boldsymbol{u} \cdot \boldsymbol{n} = \frac{\rho_{\text{water}} k}{\mu_l} \frac{\partial p}{\partial z}$$

Darcy's law $u = -(k/\mu_l)\partial p/\partial z$

How does ice grow from a hydrogel?

HYDROGEL

Clausius-Clape

The thermal problem

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

$$T = T_C \qquad \text{at } z = 0$$

$$\partial T/\partial z = 0 \qquad \text{at } z = h$$

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

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

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

ICE

$$\rho_{\text{ice}}\frac{\mathrm{d}a}{\mathrm{d}t} = -\rho_{\text{w}}$$

$T = T_C < T_m$

The gel problem

JJW & 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

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

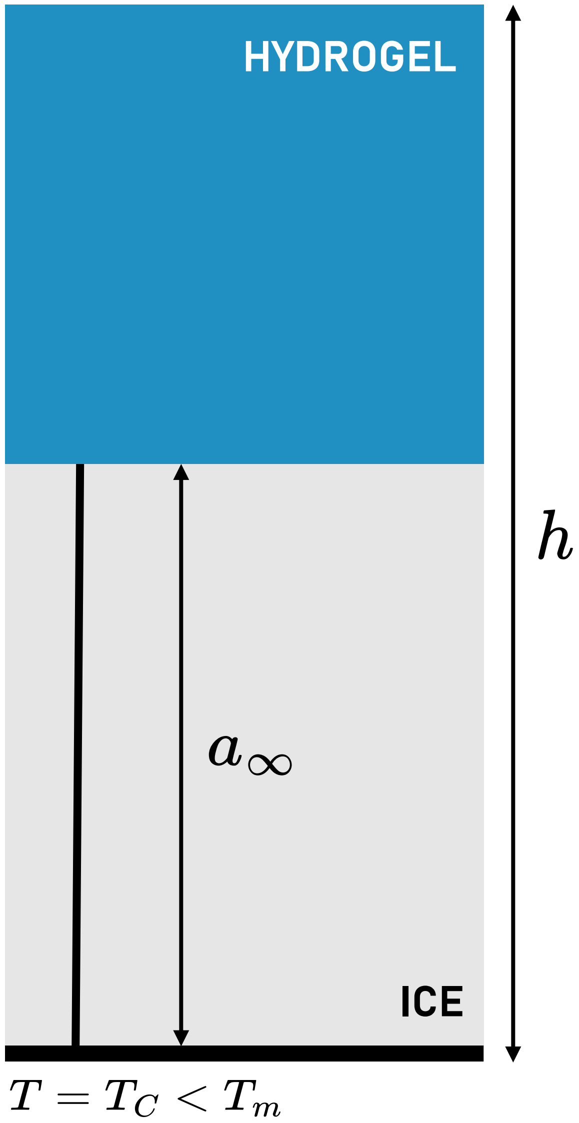
in the gel $a(t) < z < h$ — at $z = h$ — at $z = a(t)$

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

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

Darcy's law $u = -(k/\mu_l)\partial p/\partial z$

The steady state



gel dries → freezing temperature drops → $T_L = T_C$ → freezing stops

In this steady state…

- Polymer fraction is uniform (otherwise, flow from wet to dry)
- Temperature is uniformly equal to the liquidus value

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

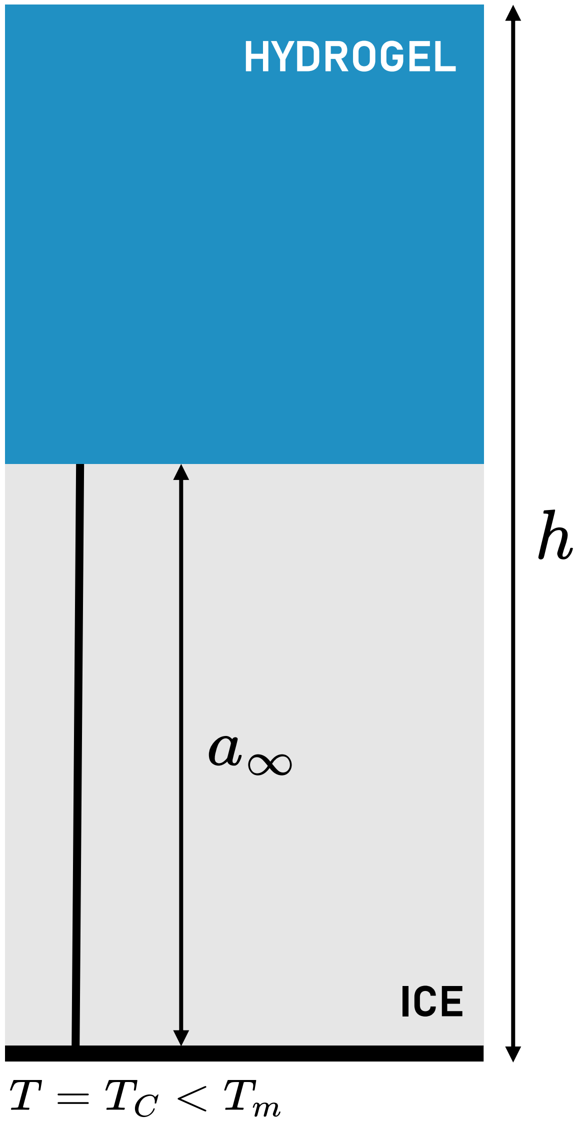
New polymer fraction comes from mass conservation
(swollen value ϕ_0) $\int_a^h \phi \, \mathrm{d}x \equiv \phi_0 h$

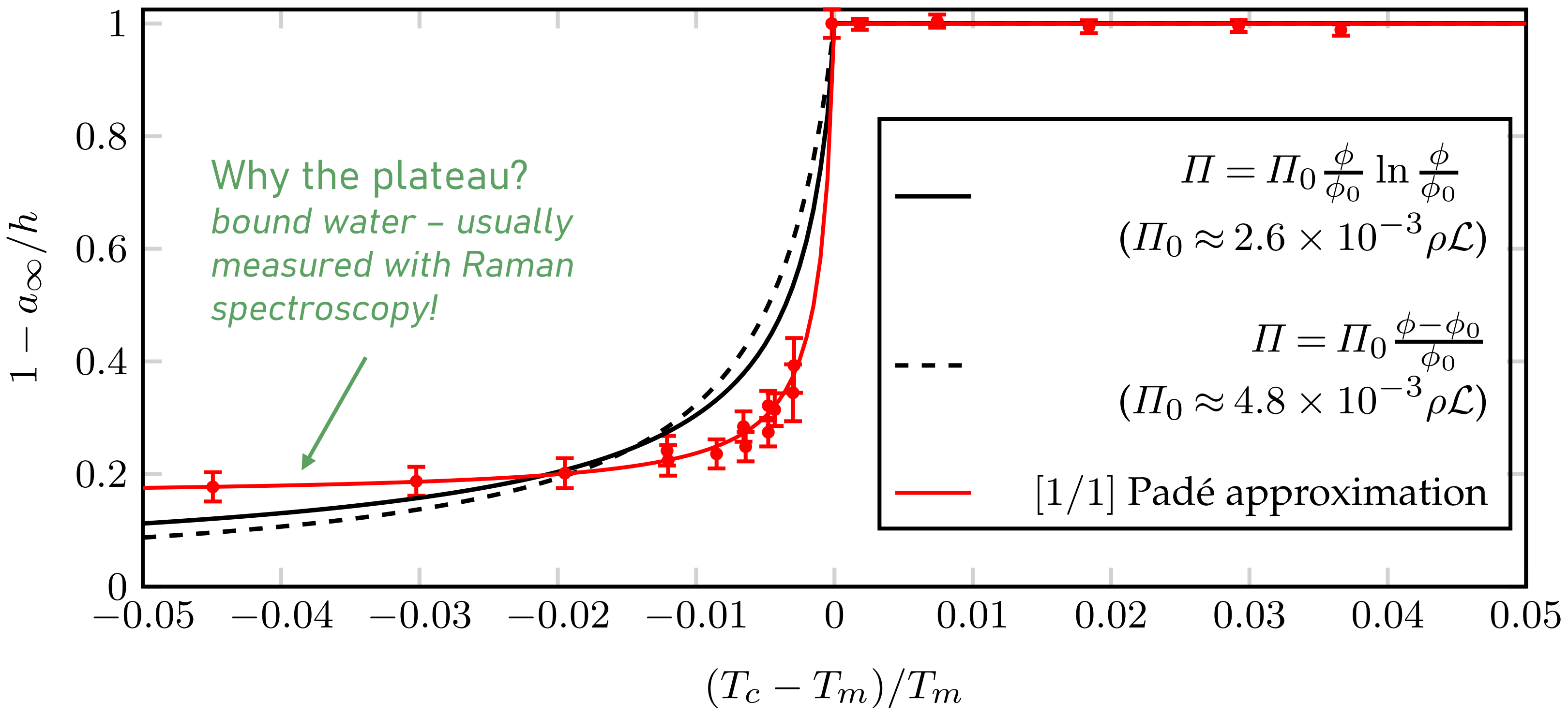
This is the basis for **Gel-freezing osmometry (GelFrO)**

Feng et al. J. Mech. Phys. Solids **201**:106166 (2025)

The steady state

data from **Feng *et al.*** J. Mech. Phys. Solids **201**:106166 (2025)



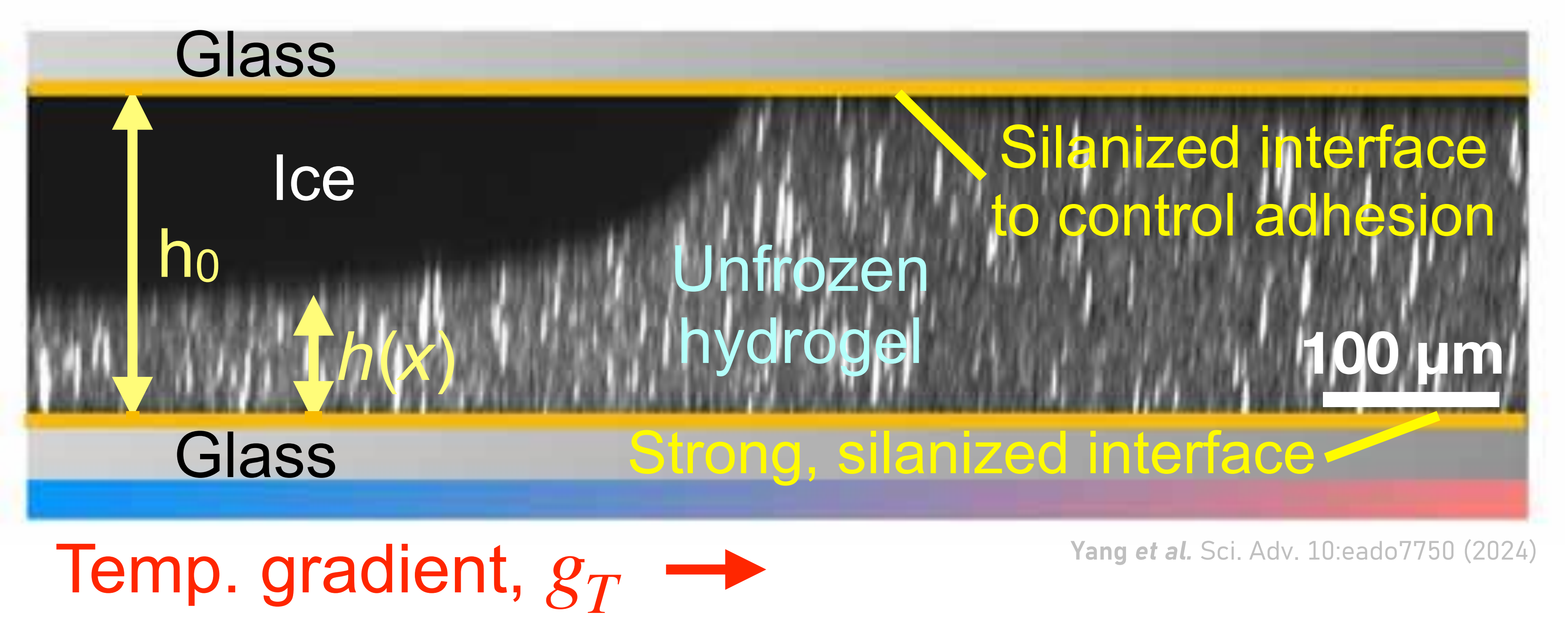


$$\Pi(\phi) = \frac{10^{-3} \rho \mathcal{L}}{\phi_0} \frac{\phi - \phi_0}{1 - \phi/(6.6\phi_0)}$$

First result: freezing gels lets us probe their internal structure, including some microscopic properties that are experimentally hard to find!

How does ice lens growth damage gels?

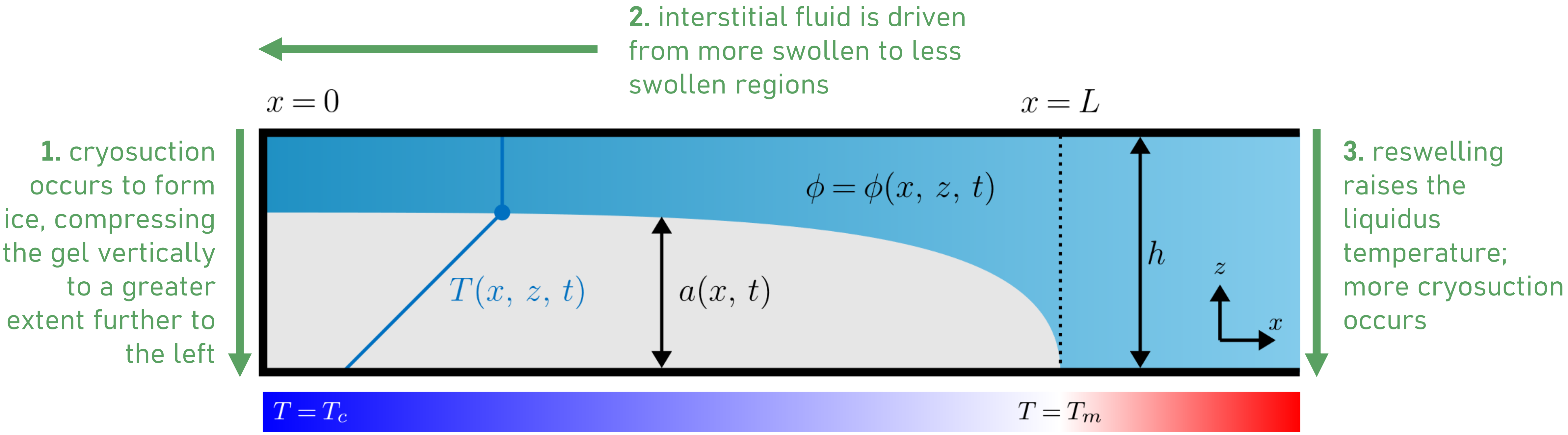
Freezing leads to stress buildup in the dried gel that remains; in our 1D example, this stress is uniform (eventually) through the gel. In 2D, however, the picture is more complicated



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

Forming ice 'lenses'

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



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 (→) ?

Modelling displacement

Gradients in pore pressure balance those in osmotic pressures **and** deviatoric (shearing) stress

$\nabla p + \nabla \Pi = 2\nabla \cdot [\mu_s(\phi)\boldsymbol{\epsilon}]$ **+** slenderness $h/L \ll 1$ **+** displacement from equilibrium $\boldsymbol{\xi} = (\xi, \eta)$

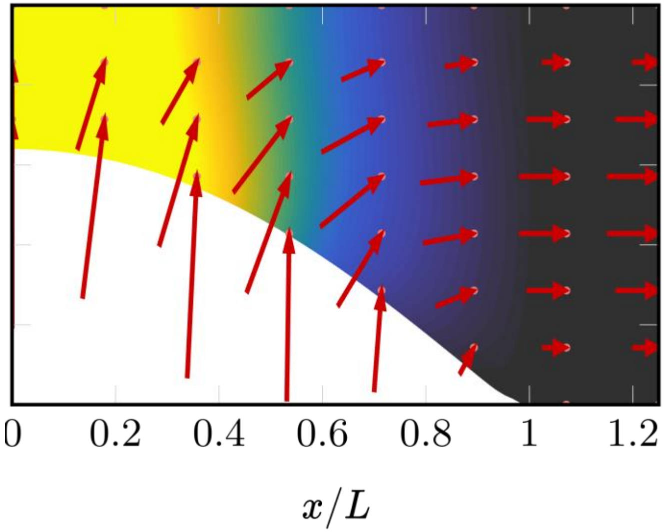
$$\nabla^4 \boldsymbol{\xi} = -3\nabla\nabla^2(\phi/\phi_0)^{1/3}$$

JJW & Worster J. Fluid Mech. 960:A38 (2023)

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

$P = p + \Pi$

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



couple with a quasi-steady temperature profile (heat diffuses faster than water)

make a choice on displacement BCs

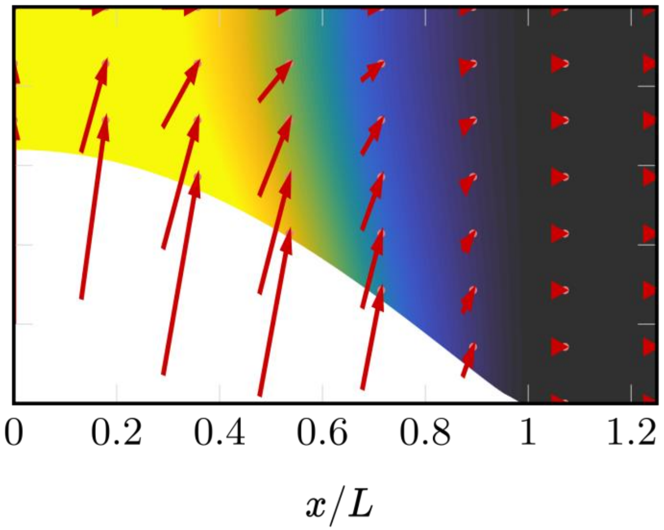
← NO-SLIP

parabolic horizontal displacement

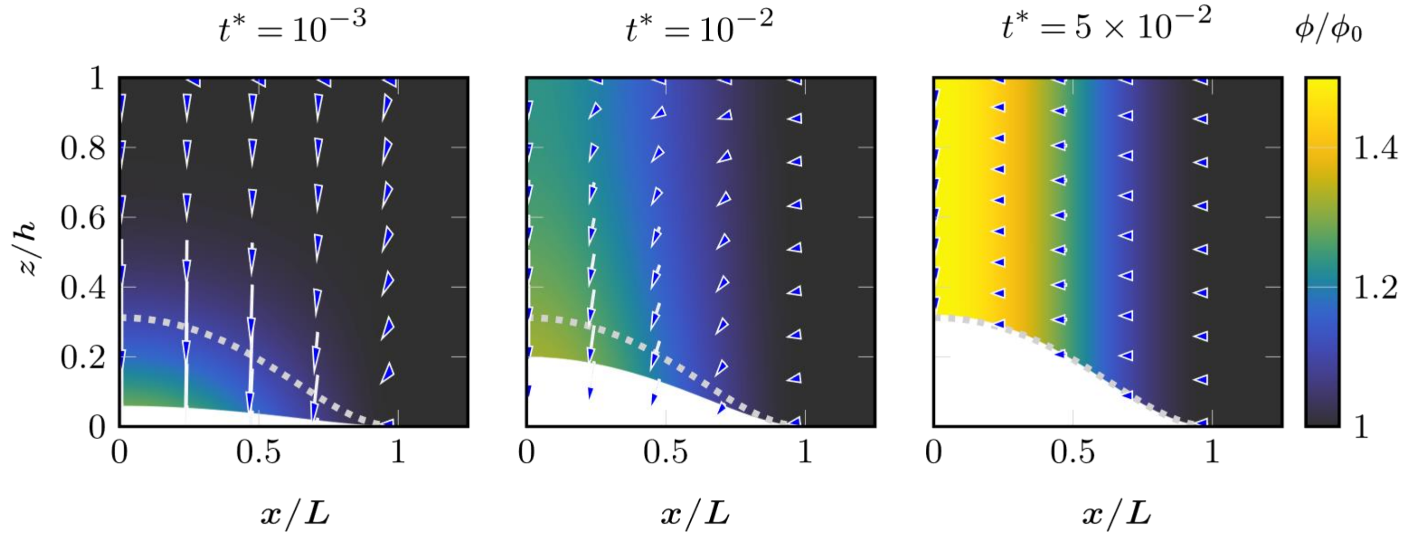
FREE-SLIP →

stretched out uniform horizontal displacement

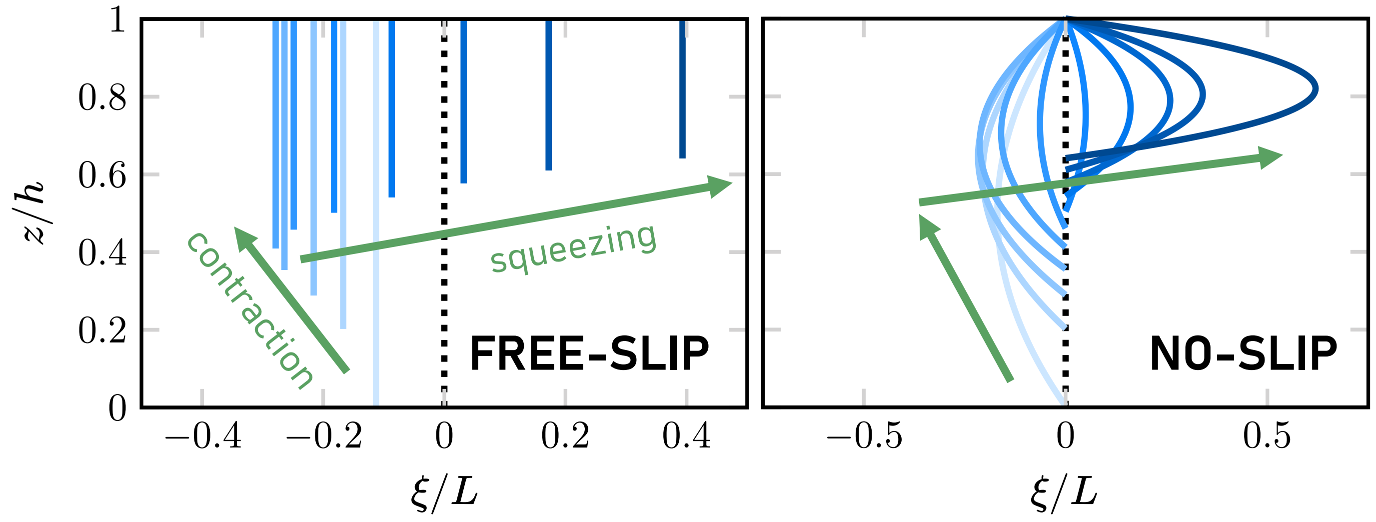
$$\xi = \int_0^x \left\{\frac{a}{h-a} - \frac{2}{h-a}\int_a^h \left[(\phi/\phi_0)^{1/2} - 1\right]\mathrm{d}z'\right\}\mathrm{d}x'$$



Dynamics of lens growth



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



Two phases of gel deformation:

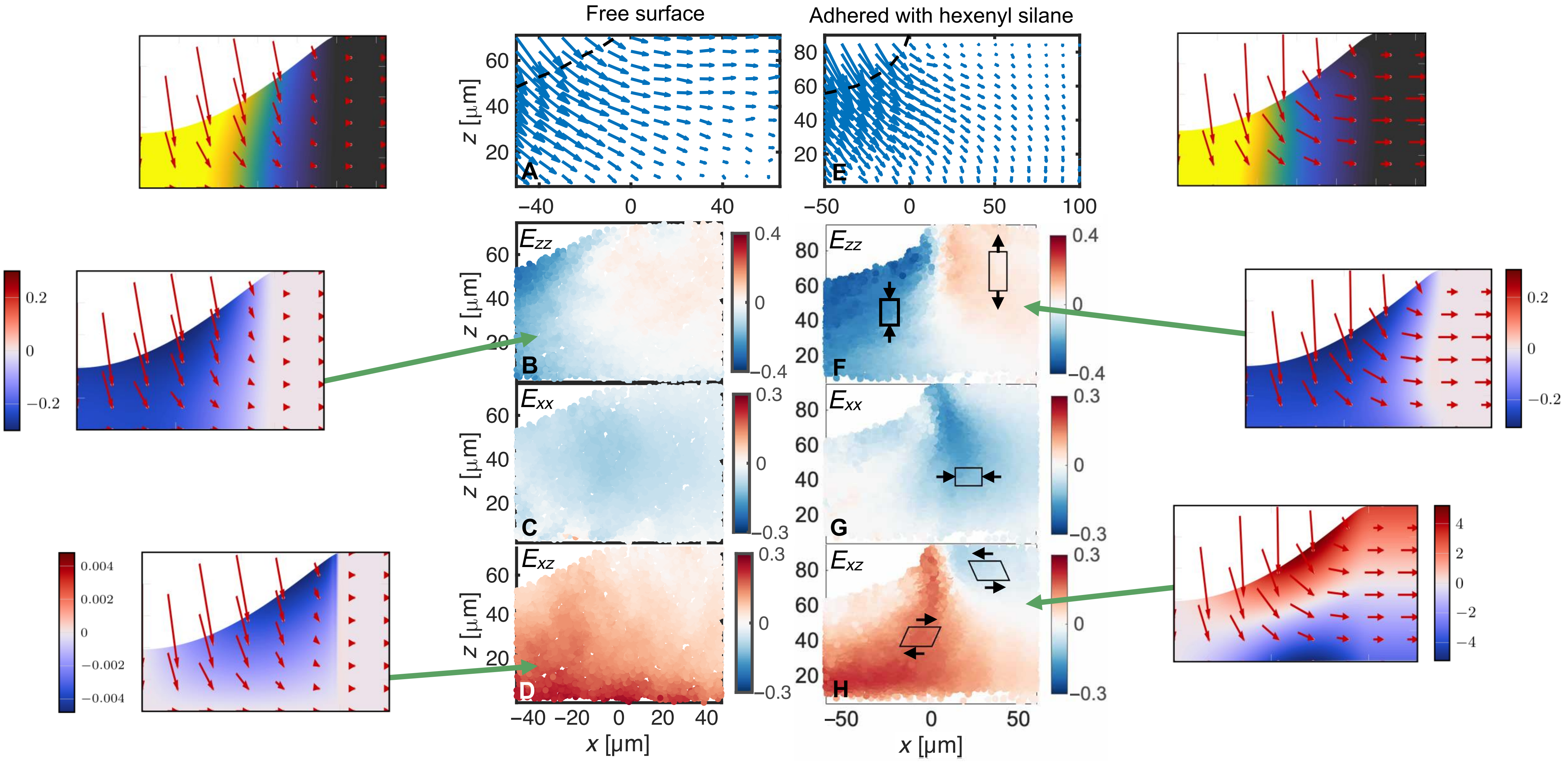
Contraction when the gel deswells, driving fluid to the ice and shrinking back in response

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

Eventually, deviatoric stresses exactly balance osmotic pressure gradients which result from

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

Stresses and strains



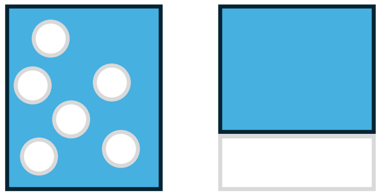
MODE I **MODE II**

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

Understanding and controlling damage

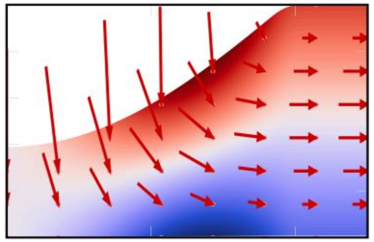
How can we minimise damage, then, to soft materials when freezing them?

- **Change the temperature:**
  dependent on whether we want to freeze water *in situ* or preserve cell structures, choose a temperature either side of the ice-entry value



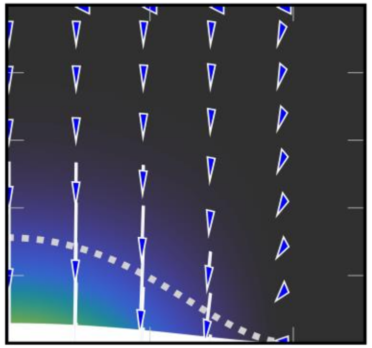
- **Change the confinement:**
  materials bound to stiff substrates build up more damage

  this is key in transplant organs, which should 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

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



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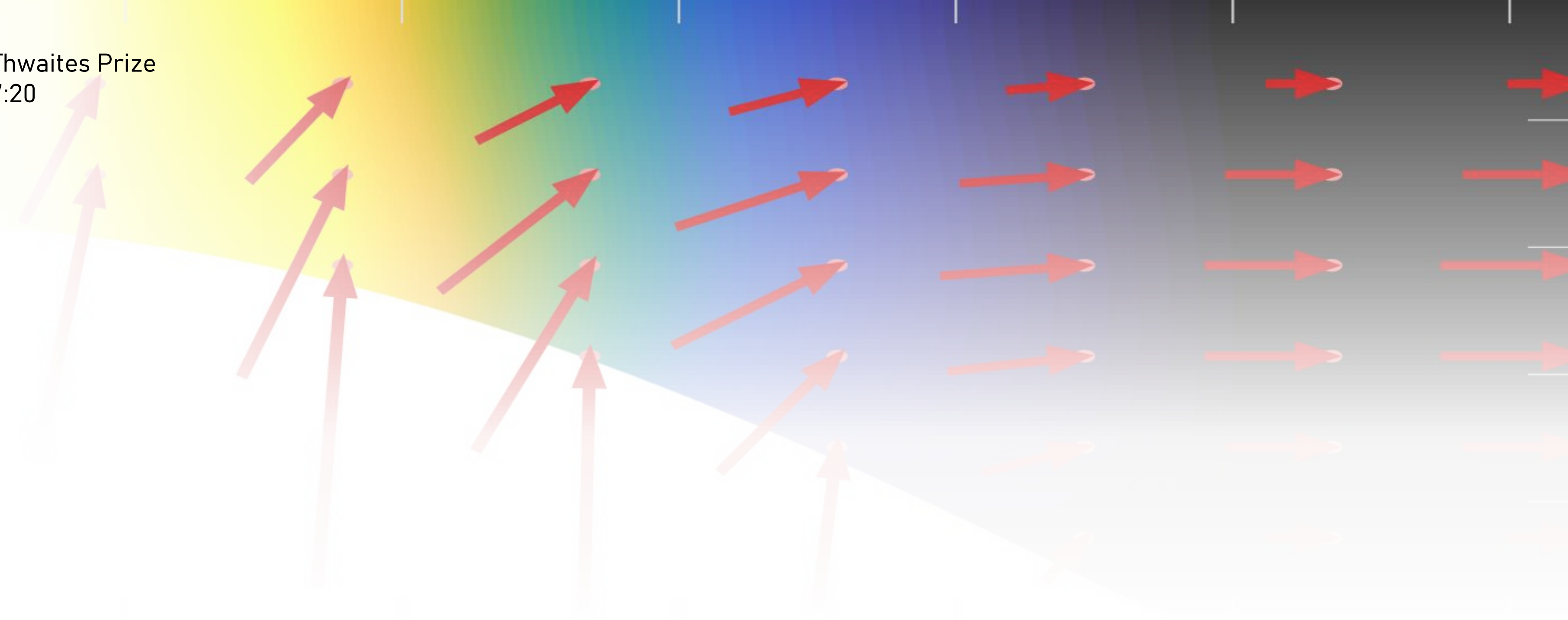

with thanks to

Grae Worster
Cambridge

Rob Style
ETH Zurich

Tom Montenegro-Johnson
Warwick


PROCEEDINGS A
Cryosuction and freezing hydrogels

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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