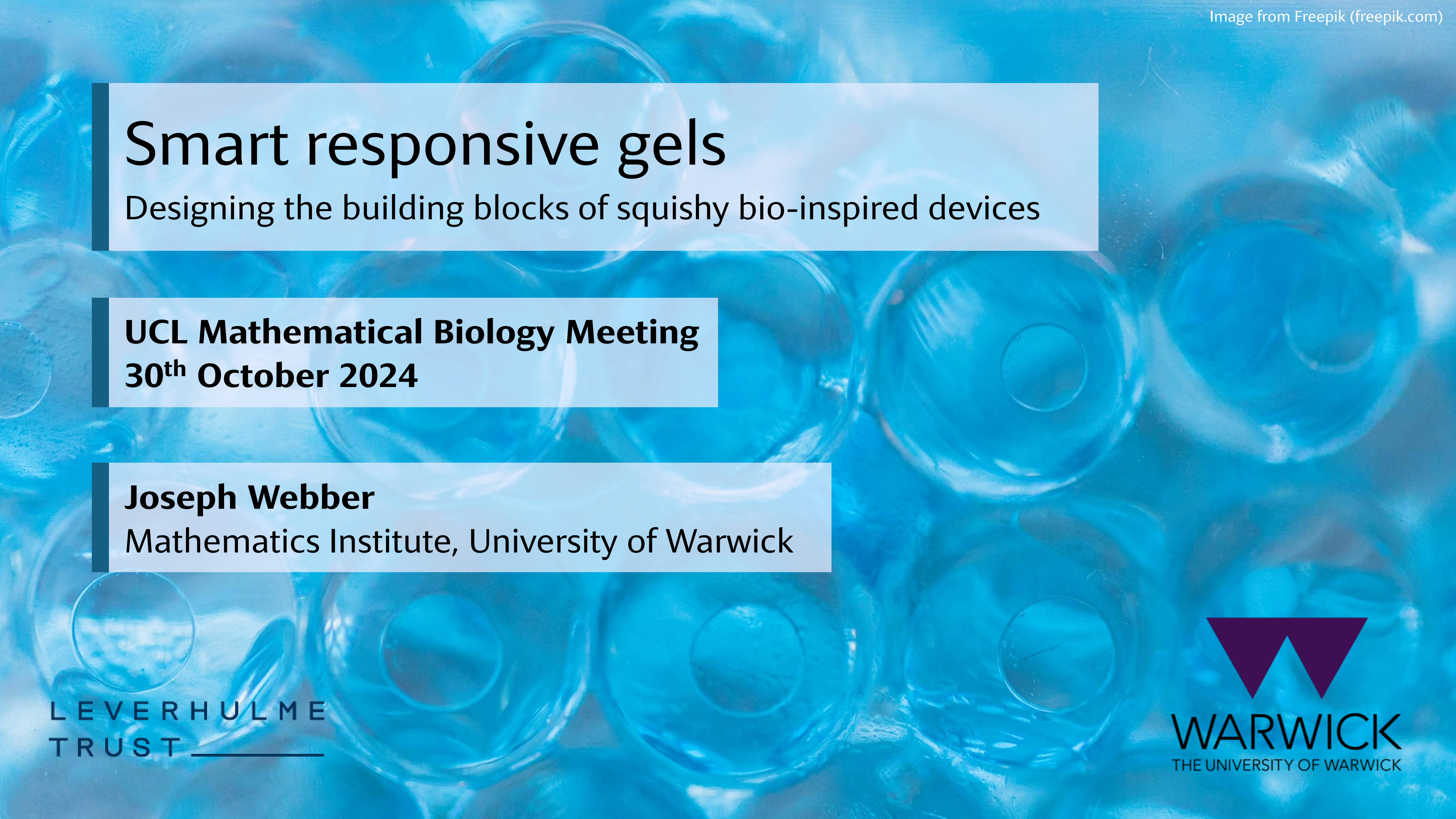
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Smart responsive gels

Designing the building blocks of squishy bio-inspired devices

UCL Mathematical Biology Meeting
30th October 2024

Joseph Webber
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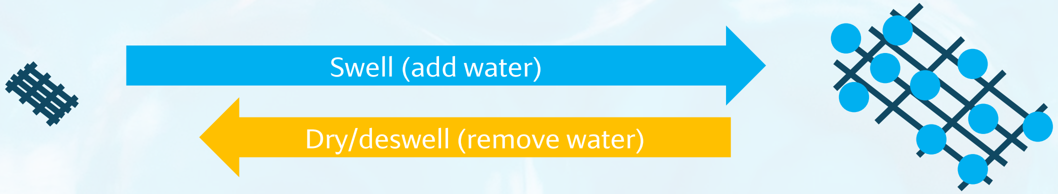
LEVERHULME TRUST

Why bother?

- Hydrogels: formed from **cross-linked** networks of **hydrophilic** polymer chains surrounded by adsorbed water molecules – often >90% water by volume



ϕ **Polymer [volume] fraction**
Ranges between >0 and 1

- Soft, squishy (low shear modulus), stretchable solids, porous in nature and can support significant interstitial flows. Easy and cheap to manufacture, but also found naturally.

- Hydrogels are found in biological tissues: collagen/cellulose/starch
- Models for biofilms?
- Water transport in vascular plants?

- Highly biocompatible owing to water content
- Drug delivery
- Tissue engineering

- “Passive” gels are everywhere: nappy filling, concrete additives, contact lenses, water retention for agriculture, evaporative cooling, …

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Hyperelastic and entropic models

- Linear poroelasticity is no good – strains of *O*(10) are possible. Need to capture nonlinearity.

$$W = \underbrace{\frac{k_B T}{2\Omega_p}\left[\mathrm{tr}\left(\mathsf{F}_{ij}\mathsf{F}_{ji}\right) - 3 + 2\log\phi\right]} + \underbrace{\frac{k_B T}{\Omega_f}\left[\frac{1-\phi}{\phi}\log\left(1-\phi\right) + \chi(\phi,\,T)(1-\phi)\right]}$$

Elastic part
(Gaussian-chain model)

- *F* is the deformation gradient tensor
- Ω_p is the volume of a single polymer chain

Mixing part
(Flory-Huggins model)

- χ is interaction parameter (hard to fit!)
- Ω_f is the volume of a single solvent (water) molecule

- Chemical potential + Thermodynamics + Darcy flow = model for gel dynamics (e.g. Cai & Suo *JMPS* 2011, Butler & Montenegro-Johnson *JFM* 2022)

Hyperelastic and entropic models

$$W = \frac{k_B T}{2\Omega_p}\left[\mathrm{tr}\left(\mathsf{F}_{ij}\mathsf{F}_{ji}\right) - 3 + 2\log\phi\right] + \frac{k_B T}{\Omega_f}\left[\frac{1-\phi}{\phi}\log\left(1-\phi\right) + \chi(\phi,\, T)(1-\phi)\right]$$

- Gives good predictions – such as the **swollen equilibrium polymer fraction** ϕ_0

- But… unsatisfactory for a number of reasons:
  - Messy system of lots of equations: needs numerical solution
  - What motivates our elastic or mixing models? Are they valid?
  - Steady states: easy. Transient behaviour: hard.
  - **Fitted parameters don't easily correspond to macroscopically-measurable phenomena**

- Some other approaches have been taken to fix this:
  - Large-strain poroelasticity (Bertrand et al., *Phys Rev Appl* 2016)
  - Linear poroelasticity for small swelling (Doi, *J Phys Soc Jpn* 2009)

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LENS modelling

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

- **Key idea:** allow for nonlinearity in isotropic strains corresponding to swelling/deswelling but linearise around deviatoric strains that must be small. Measure all displacements relative to the fully-swollen equilibrium.

Displacement from equilibrium

Small deviatoric part

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

Cauchy strain

Isotropic part just due to swelling

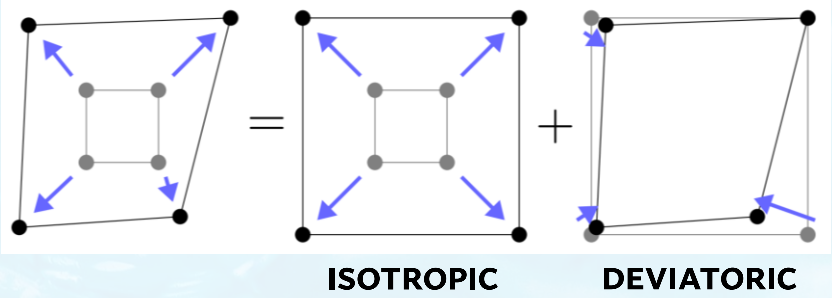
Shear modulus

$$\underset{\uparrow}{\boldsymbol{\sigma}} = -P\mathbf{I} + 2\overset{\downarrow}{\mu_s}(\phi)\boldsymbol{\epsilon}$$

Cauchy stress

- Pressure is taken to have contributions from the water phase, hydrophilic effects, and bulk (isotropic) elasticity, so take $P = p + \Pi$

- p is the **pervadic**, **pore**, or **Darcy** pressure
- Π is the **generalised osmotic pressure**



LENS modelling

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

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

Permeability

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

Interstitial fluid flux

Viscosity

- A gel, swollen to any degree, can be described using three material parameters: a **shear modulus** $\boldsymbol{\mu_s(\phi)}$, an **osmotic pressure** $\boldsymbol{\Pi(\phi)}$ and a **permeability** $\boldsymbol{k(\phi)}$

- This treats the gel as linear elastic with (potentially) nonlinear properties, each of which is macroscopically meaningful:

    - The shear modulus governs the initial incompressible response to forcing
    - The osmotic pressure governs the steady state reached where water is expelled or drawn in
    - The permeability sets the timescale over which an adjustment occurs

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LENS modelling

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JFM, 2023

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

Combine with conservation of water, conservation of polymer, and force-free momentum balance

Phase-averaged flux
of water and polymer

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

Slow nonlinear diffusion of water

Note: we have not prescribed constitutive laws, and can in fact deduce forms of the three parameters given, say, Flory-Huggins theory and Gaussian-chain elasticity

LENS modelling

Webber & Worster *and*
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JFM, 2023

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

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Slow nonlinear diffusion of water

In general, need another piece of the puzzle (*Webber, Etzold & Worster, JFM 2023b*) to find displacement field $\nabla^4\boldsymbol{\xi} = -3\boldsymbol{\nabla}\nabla^2(\phi/\phi_0)^{1/3}$

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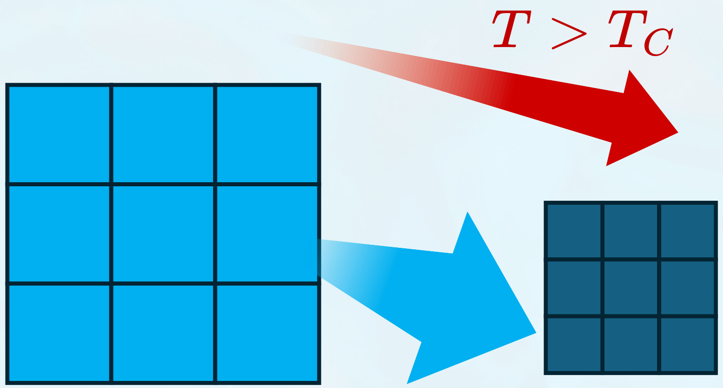
Responsive gels

- Gels can be engineered to respond to a number of external stimuli: heat, light, pH, chemical concentration...

- Thermo-responsive gels have a **lower critical solution temperature (LCST)** above which the polymer rapidly loses its affinity for water, leading to shrinkage. This process is reversible.

- Usually modelled by having a temperature-dependent Flory chi parameter, measuring the strength of intermolecular interactions between polymer and water
    - Constrains us to messy nonlinear approaches
    - Microscopic modelling is hard
    - Many different parameters to fit (Butler & Montenegro-Johnson, *JFM* 2022)



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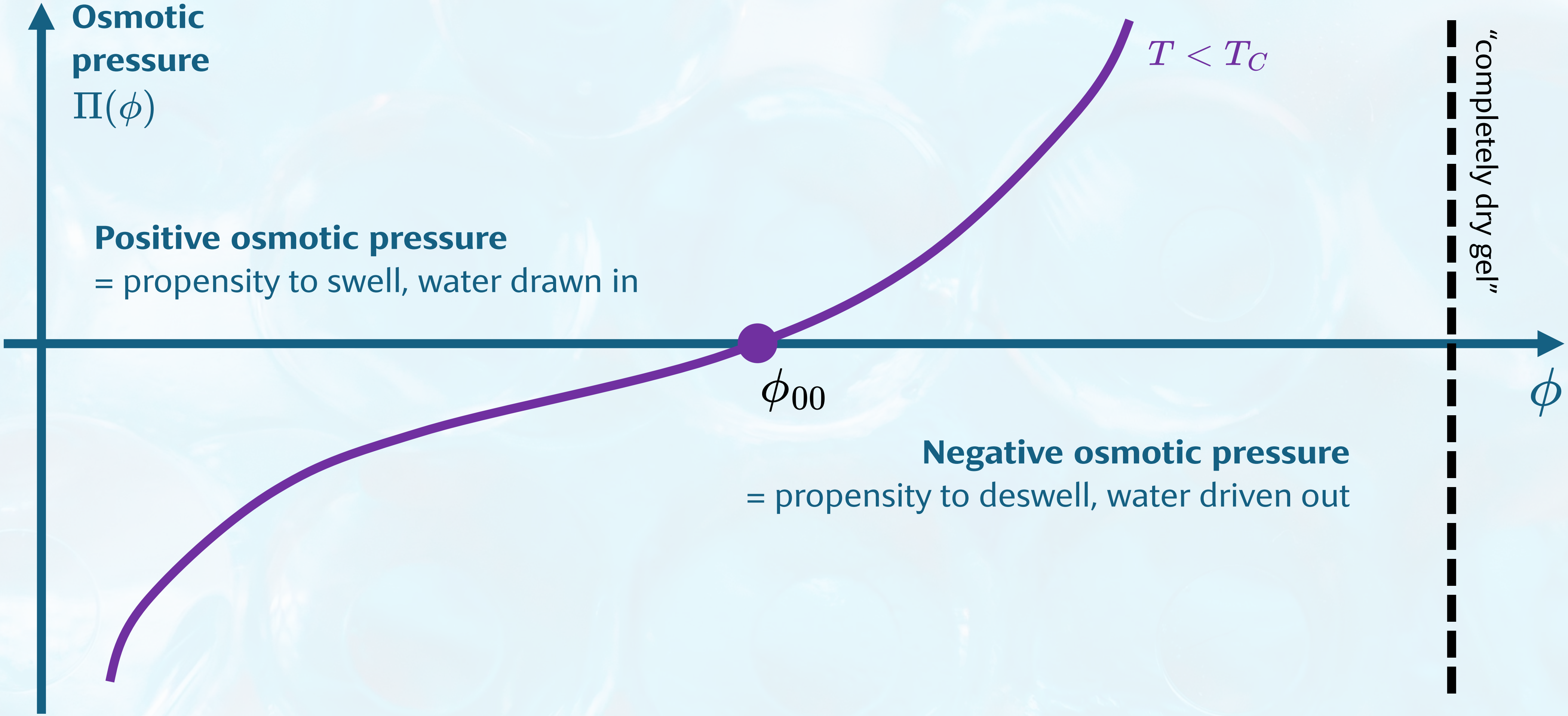
(Thermo-/chemo-/photo-)responsive LENS



Positive osmotic pressure
= propensity to swell, water drawn in

Negative osmotic pressure
= propensity to deswell, water driven out

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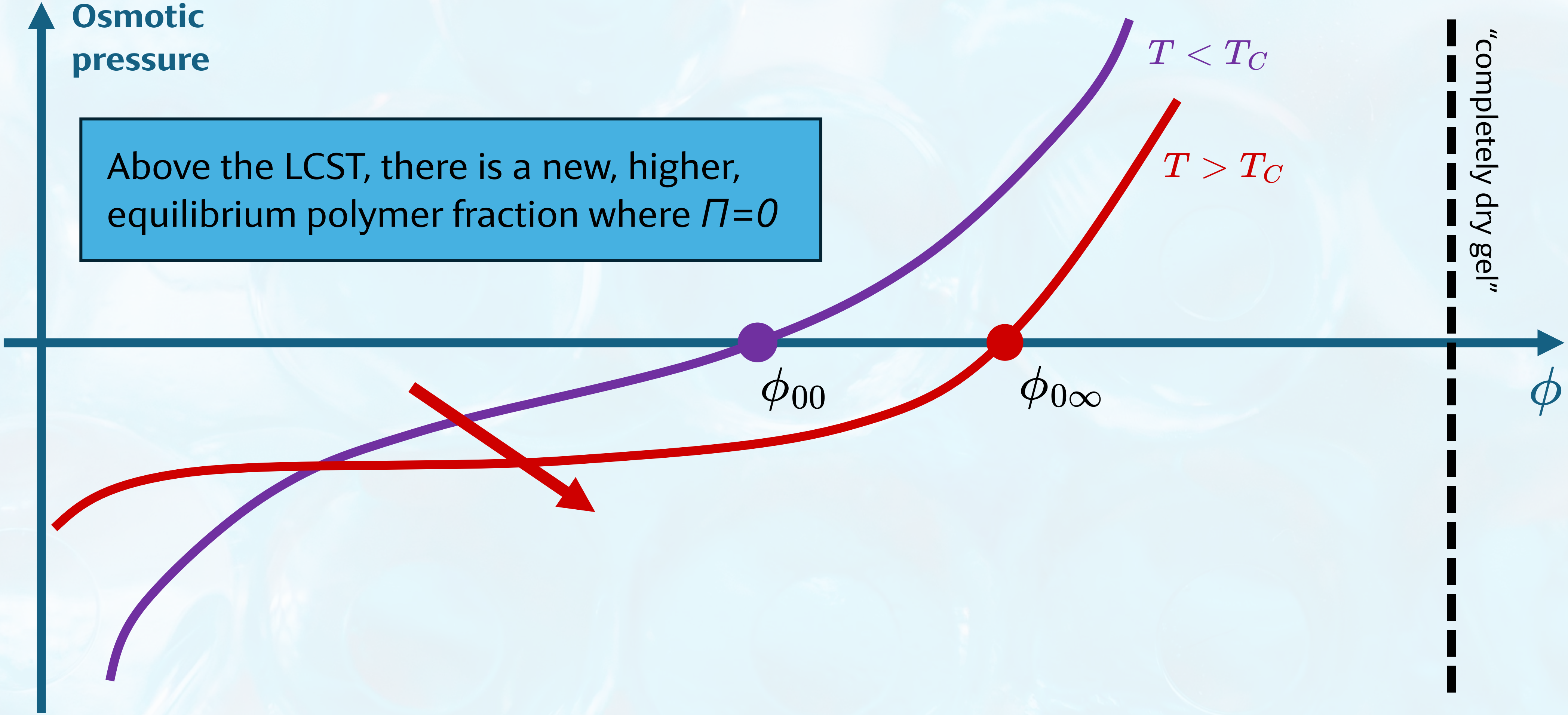
(Thermo-/chemo-/photo-)responsive LENS



Above the LCST, there is a new, higher, equilibrium polymer fraction where *Π=0*

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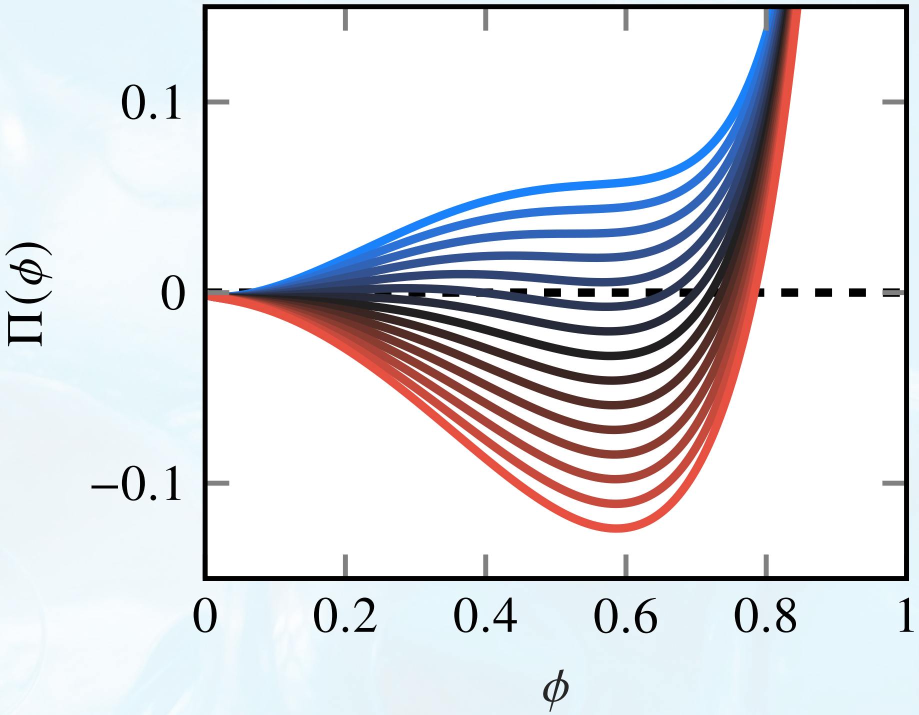
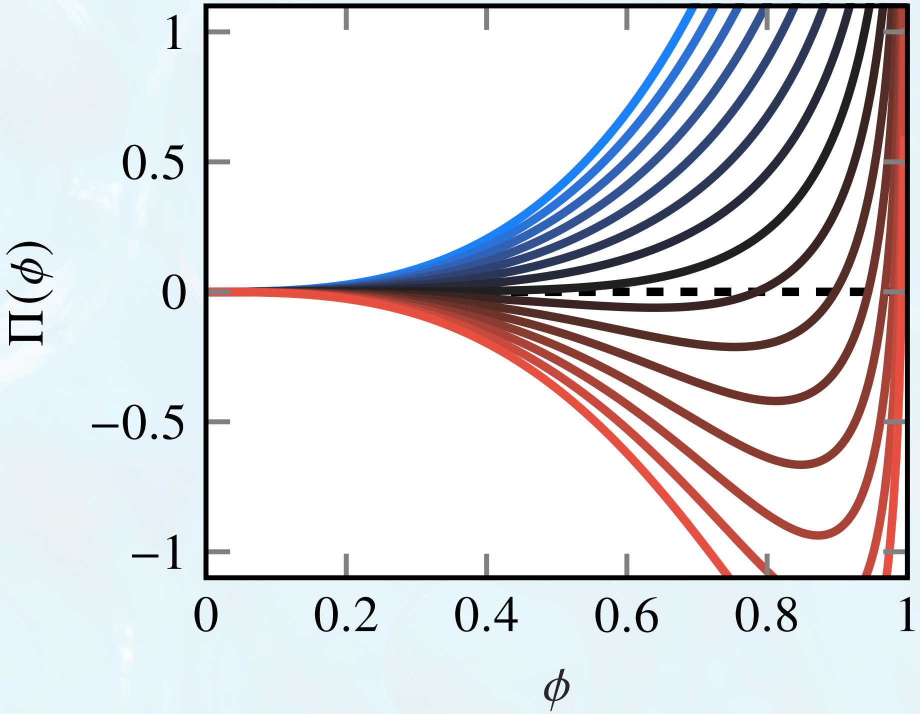
(Thermo-/chemo-/photo-)responsive LENS

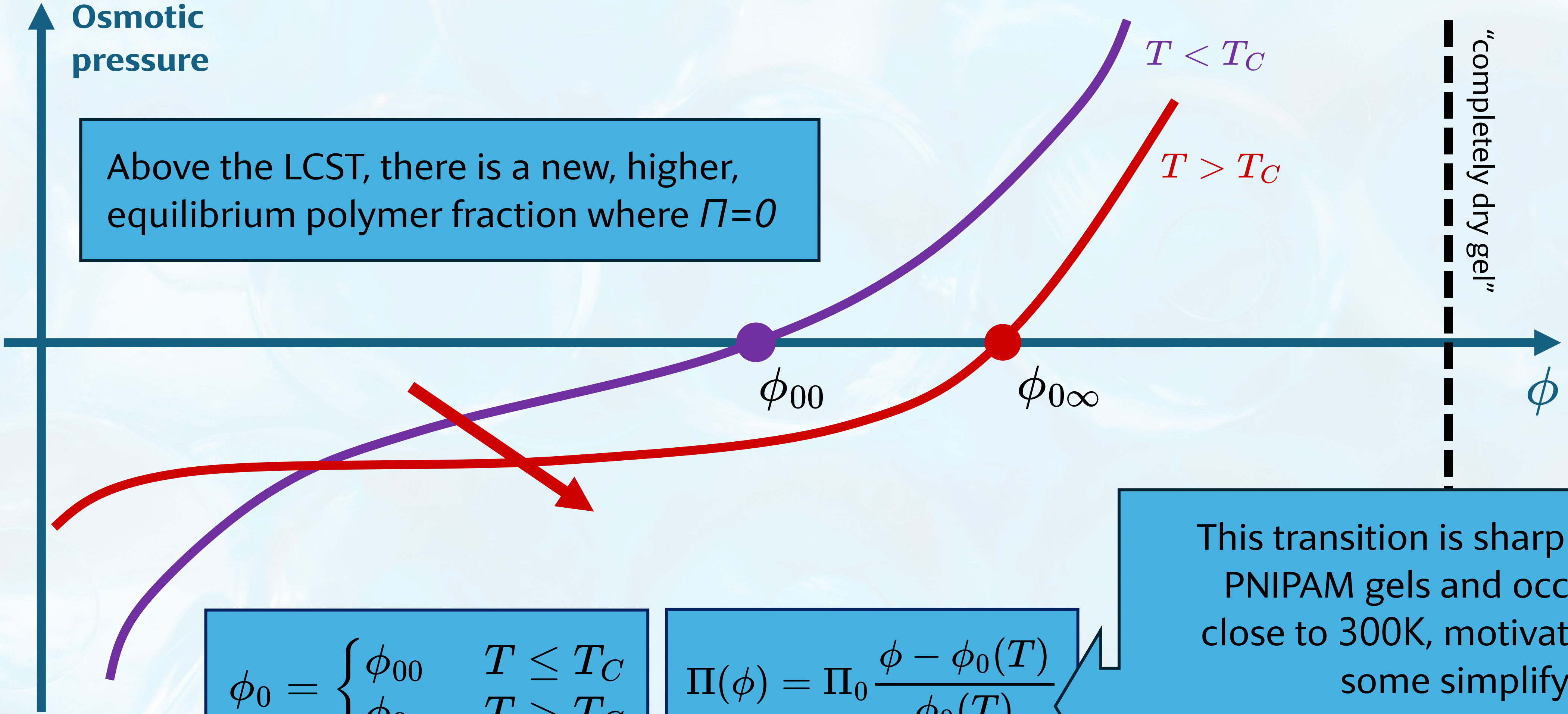


(a) ANB parameters



(b) HHT parameters

(Thermo-/chemo-/photo-)responsive LENS



Above the LCST, there is a new, higher, equilibrium polymer fraction where *Π=0*

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

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

This transition is sharp for PNIPAM gels and occurs close to 300K, motivating some simplifying assumptions on *Π*

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Smart gels as machines

Sensors

- Can convert changes in the local environment to changes in shape
- Changes are **large** and **predictable**

e.g. a gel membrane becomes impermeable when a chemical concentration is high enough.

Actuators

- Programmable shape change is possible *via* swelling or deswelling
- Thermoresponsive gels can be impregnated with gold nanoparticles, and lasers lead to heating and deswelling

e.g. soft robotic grippers or valves that can be opened or closed

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Smart gels as machines

Sensors
- Can convert changes in the local environment to changes in shape
- Changes are **large** and **predictable**

e.g. a gel membrane becomes impermeable when a chemical concentration is high enough.

Computers
Take input from sensors and use it to control actuators. Logic circuits make decisions and can provide feedback mechanisms.

e.g. artificial pancreas, smart pumps, hygrostat logic circuits,...

Actuators
- Programmable shape change is possible *via* swelling or deswelling
- Thermoresponsive gels can be impregnated with gold nanoparticles, and lasers lead to heating and deswelling

e.g. soft robotic grippers or valves that can be opened or closed

...all in one gel component?

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Missing pieces: two gaps

- Gels are already being used as actuators, and microfluidic devices employ thermo- and chemo-responsive mechanisms

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

~10^{-3} kg m^{-1} s^{-1}

$$t_{PE} \sim \frac{\mu_l L^2}{\Pi_0 k}$$

~10^{4} kg m^{-1} s^{-2}

~10^{-15} m^{2}

- For second-scale responses, need $L \sim 10^{-4}$ m, which constrains us to microfluidics.

- We also have no way to communicate information between gel devices: computers require networking or connections between sensor and actuator to function.

- **Both of these problems can be unlocked using the modelling we've already introduced**

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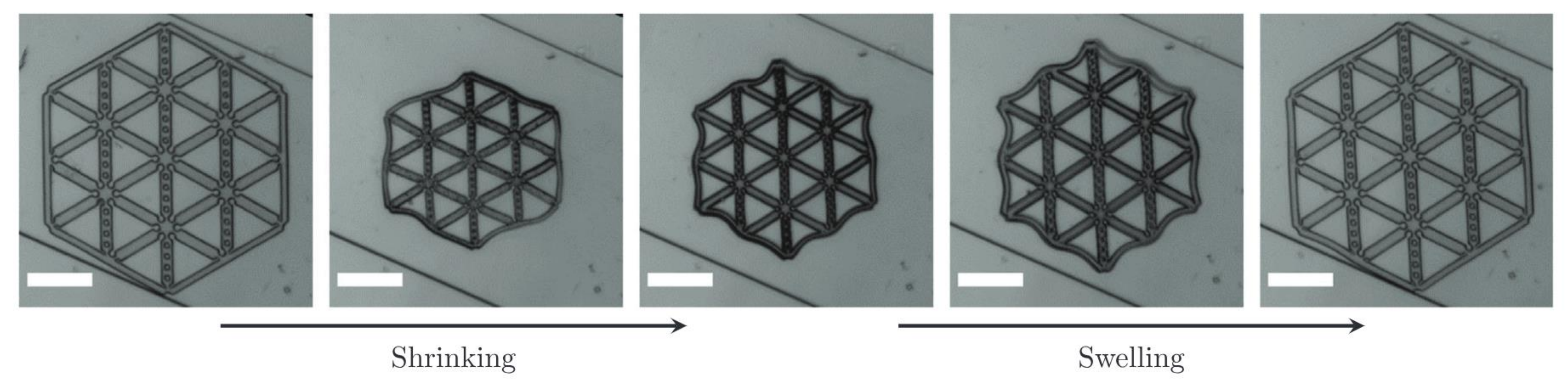
Problem 1: responsive gels are slow

Building displacement pumps from hydrogel tubes

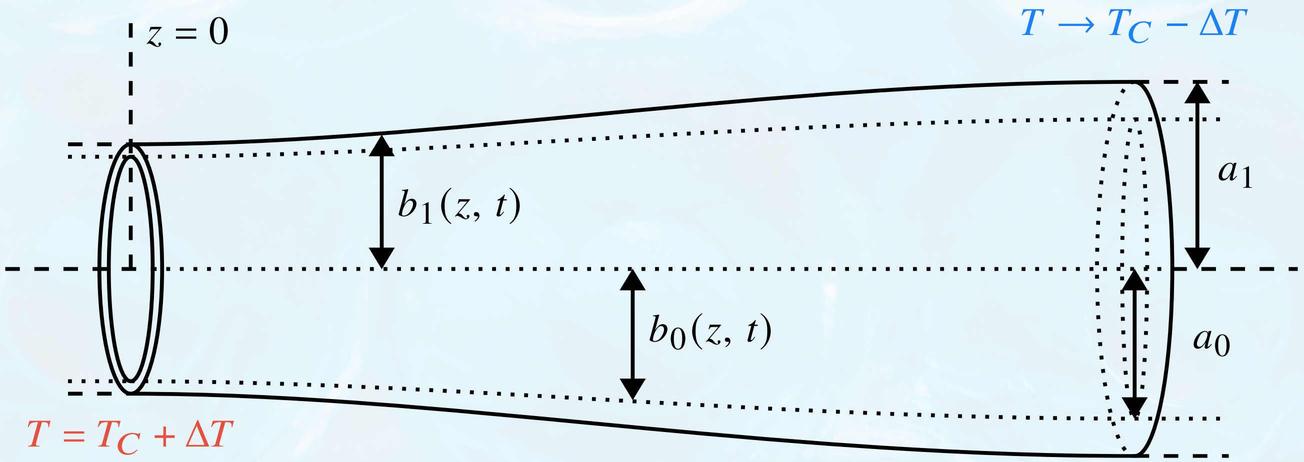


Maslen *et al. Macromol Rapid Commun* 2022

Image from Freepik (freepik.com)

Porous media as a network of tubes

- Swelling and deswelling is more rapid when micropores are drilled into the gel structure, since the movement of water is no longer constrained by slow diffusion through the nanopores
- This technique has been used to make faster actuators (Spratte *et al. Adv Intell Syst* 2022, Maslen *et al. Macromol Rapid Commun* 2022)
- Can't just use a scaling argument to find how drilling micropores will affect response times; need to model the whole system! This hard traditionally, with a complex geometry, and perhaps easier with LENS



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Displacement modelling

- To make modelling easier, take a slenderness assumption $\varepsilon = a_1 / L \ll 1$

- Assume that the deswelling is locally isotropic, and therefore

$$\frac{b_1}{a_1} = \frac{b_0}{a_0} = \left(\frac{\phi}{\phi_{00}}\right)^{-1/3}$$

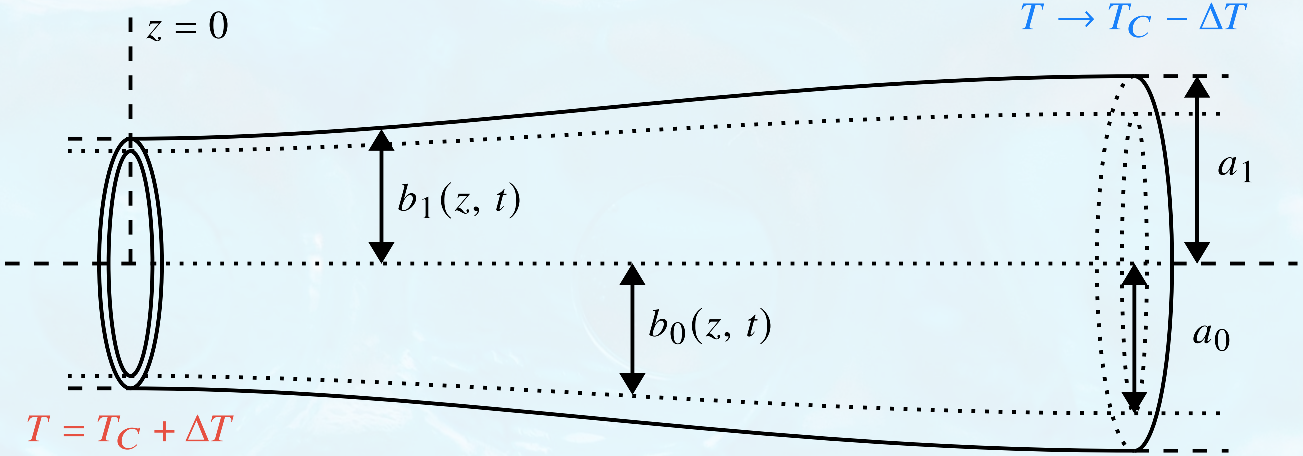
where ϕ is the polymer fraction on the inside of the tube, at leading order.

- Take

=0 on inside of tube

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

Found by plugging in to diffusion equation and scaling (sep. variables)



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Polymer fraction evolution

- Separation of variables implies that we must just solve for ϕ_1, with the radial structure function deduced from boundary conditions on the outside of the tube:

$$\frac{\partial\phi_1}{\partial t} + q_z\frac{\partial\phi_1}{\partial z} = f(z,\, t,\, T) + \frac{\partial}{\partial z}\left[D(\phi_1,\, T)\frac{\partial\phi_1}{\partial z}\right]$$

Total (phase-averaged) flux

Separation “constant”

Nonlinear diffusivity

$$\phi_2 = \frac{f(z,\, t,\, T)}{4D(\phi_1,\, T)}\left[r^2 - \frac{\ell^2(\phi_1/\phi_{00})^{-2/3}}{\log\ell + \log\left[(\phi_1/\phi_{00})^{-1/3}\right]}\right]$$

Thinness of tube

a_0 / a_1

- Boundary conditions arise from:
  - Decay in perturbations from equilibrium as $z \to \infty$ ($\partial\phi/\partial z \to 0$)
  - Symmetry around $z=0$ ($\partial\phi/\partial z = 0$)
  - No stress on outer boundary ($\phi = \phi_0(T)$ on $r=b_1$) which gives

$$f(z,\, t,\, T) = \frac{4D(\phi_1,\, T)}{\varepsilon^2}\left(\frac{\phi_1}{\phi_{00}}\right)^{2/3}\frac{3\log\ell - \log\left(\phi_1/\phi_{00}\right)}{3\log\ell - (1-\ell^2)\log\left(\phi_1/\phi_{00}\right)}\left[\phi_0(T) - \phi_1\right]$$

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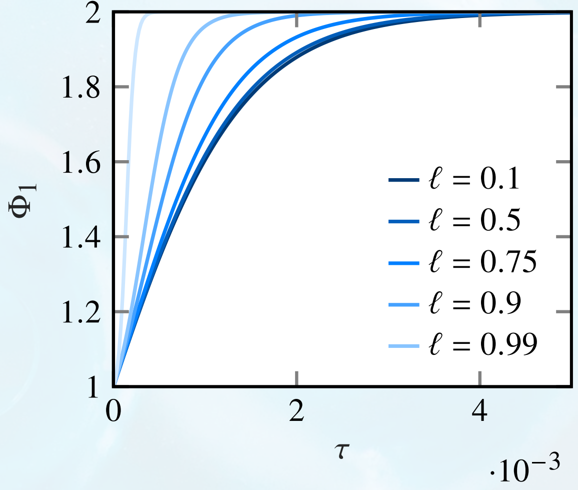
Heat transfer

$\Phi = \phi / \phi_{00}$



- We have a model for the response of a tube to a time- and space-varying temperature field *T(z, t)*
- If we instantaneously raise the temperature above the LCST, water is expelled into the lumen and into the surroundings and the tube collapses uniformly (flows are a second-order effect that don't change the dynamics in a thin tube)
- Introduce the Lewis number *Le* which is the ratio of heat diffusivity to compositional diffusivity. For these tubes, *Le ~ 10-100* and so we make the large-*Le* approximation that a heat pulse is purely diffusive

$$\frac{\partial T}{\partial z} = \kappa \frac{\partial^2 T}{\partial z^2}$$

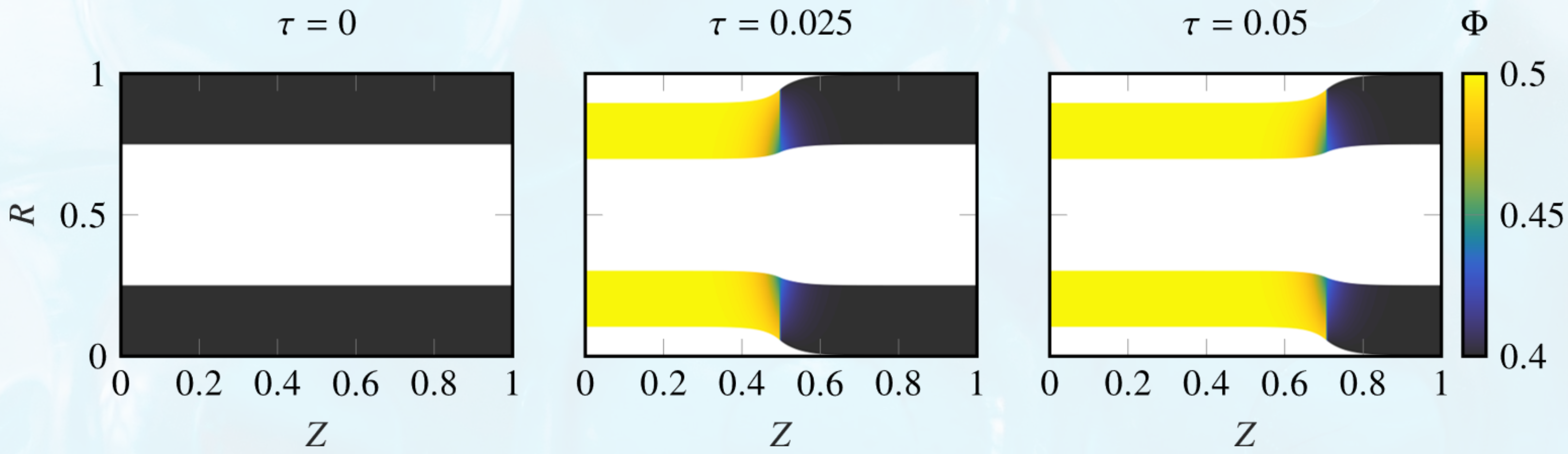
$$\begin{cases} T(z,\, 0) = T_C - \Delta T \\ T(0,\, t) = T_C + \Delta T \\ \partial T / \partial z \to 0 \text{ as } z \to \infty \end{cases}$$

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

Step/*tanh* approximation

- Non-dimensionalise: times on the poroelastic timescale, axial lengths on the lengthscale *L*, radial lengths on a_1
- The heat front (behind which the temperature is above the LCST) is given by

$$Z_C(\tau) = 2\,\mathrm{erfc}^{-1}\left(\frac{1}{2}\right)\sqrt{Le\,\tau}$$



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

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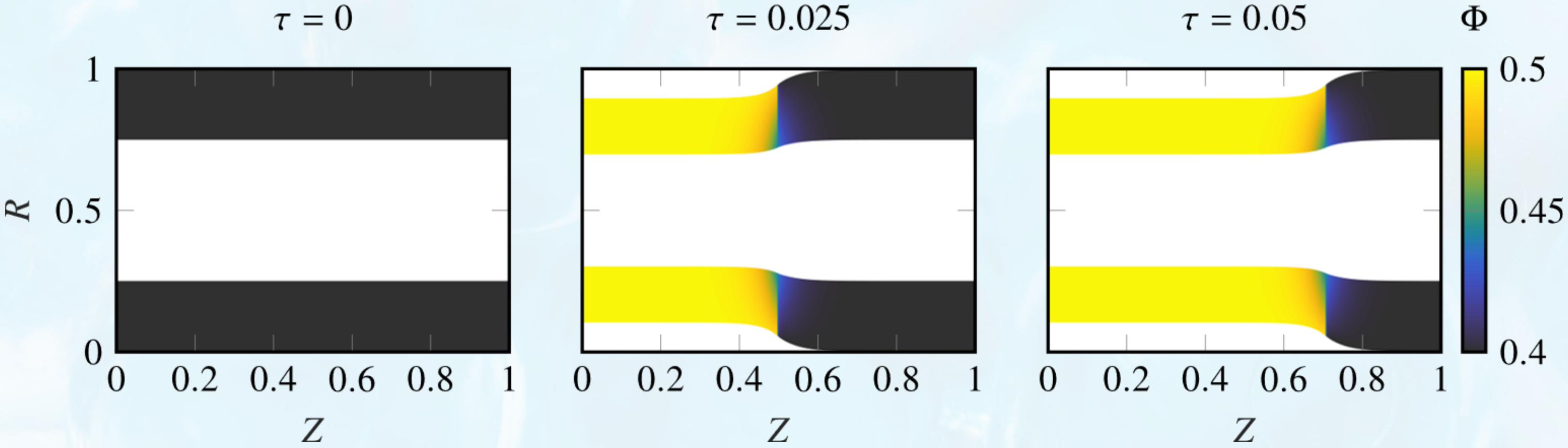
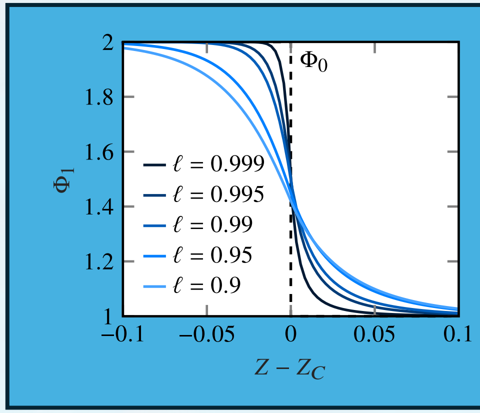
Step/*tanh* approximation



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



$$A(\ell) \propto (1 - \ell)^{-1/2}$$

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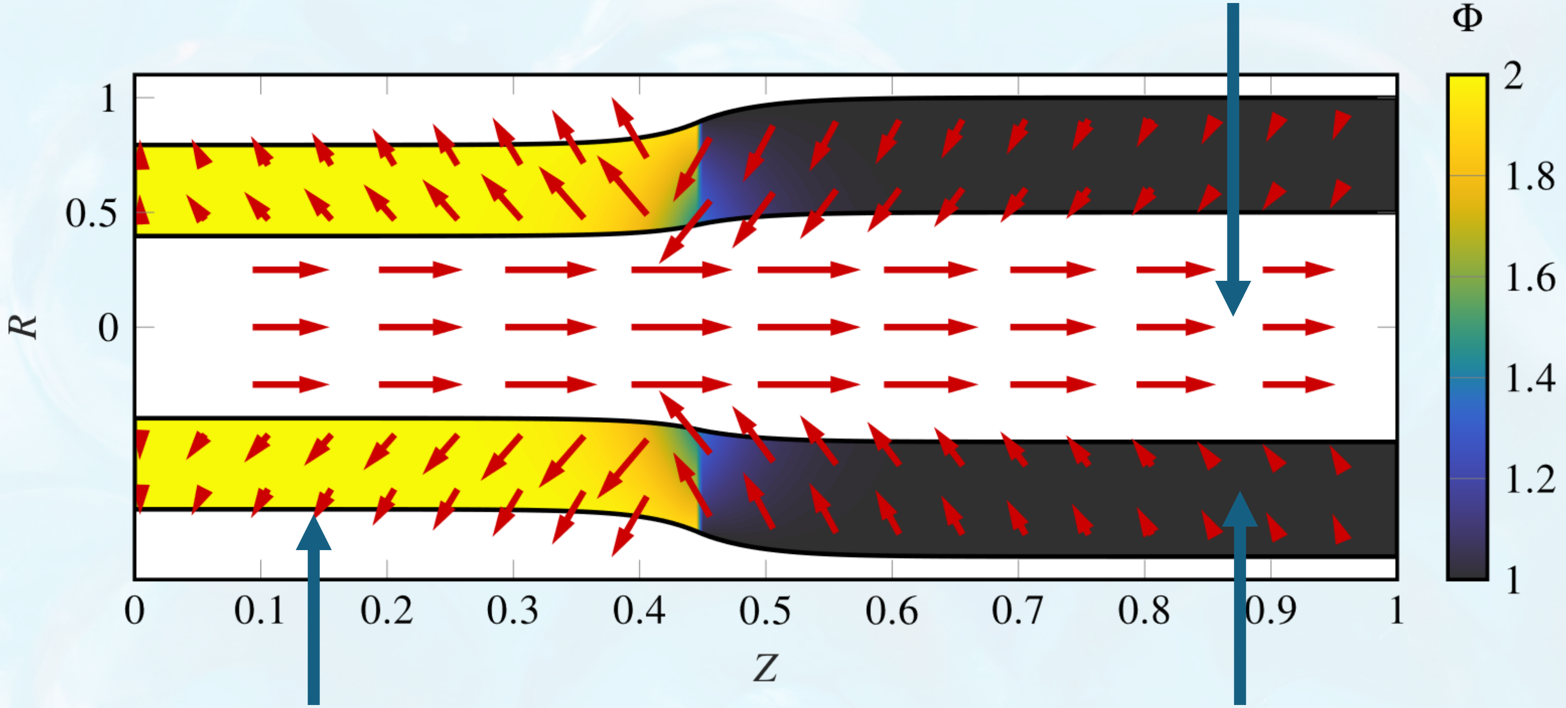
Flows in the gel

Flows through the lumen

Poiseuille flow driven through the middle; fastest, given by "squeezing" fluid out of place

$$p + \Pi(\phi_1) = 0$$
$$\Rightarrow p = \Pi_0(1 - \phi/\phi_0(T))$$



Flows out of the gel and into the surrounds

The principal route for water loss – the outside instantaneously dries and interstitial flows are sent towards the drier gel regions

Flows through the gel

Very slow, with limited net flux since the tube is thin and transport is mediated by the low permeability

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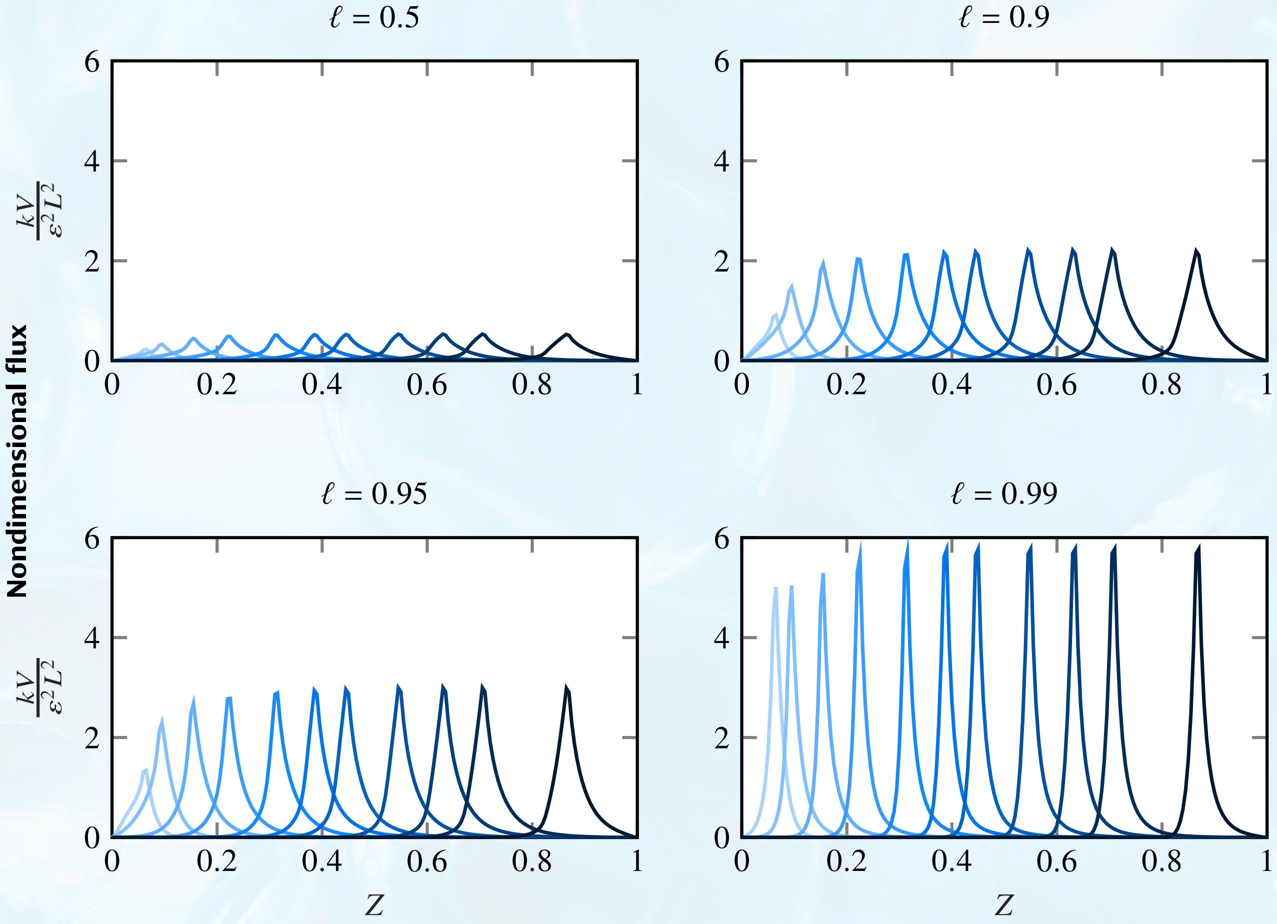
Fast(ish) flows in the lumen



- Thinner tubes have a faster response and so lead to larger peak velocities at the deswelling front

- However, the sharpness of the profile is greater when ℓ → *1* so the total integrated transport is approximately constant in ℓ

- Have an expression for fluxes and response times:
  - Chain together to make porous media
  - Scaling law from many joined tubes

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Problem 2: responsive gels don’t talk

Oscillating reactions lead to communication

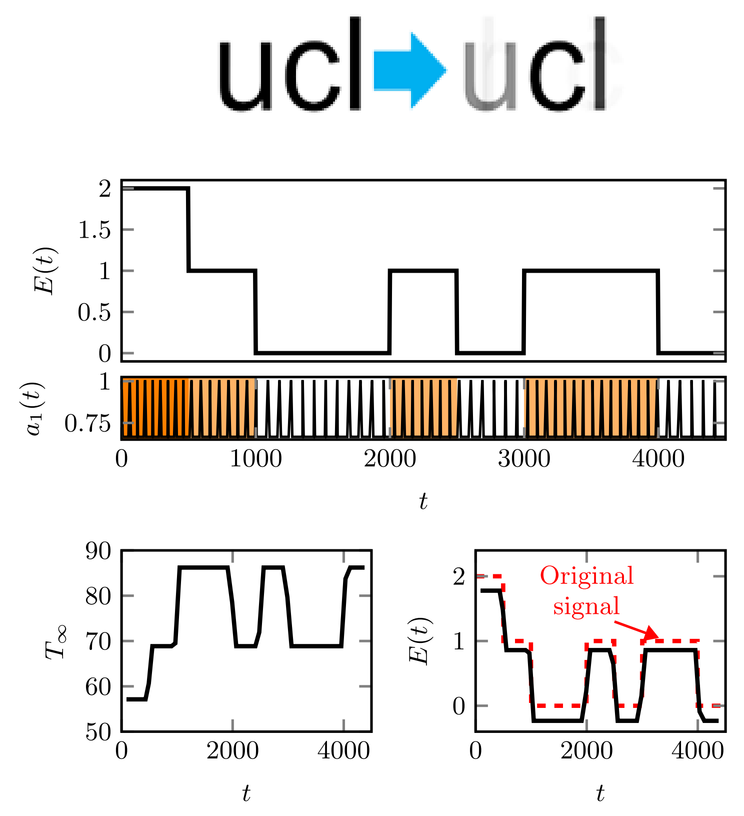

Image from Freepik (freepik.com)

The BZ reaction

- There are very few chemical reactions that naturally oscillate with a predictable period, and even fewer that are (relatively) straightforward to model mathematically
- The BZ (Belousov-Zhabotinsky) reaction was discovered in the mid-20th century and is often modelled using reduced systems of autocatalytic reactions
- In this proof-of-concept, we will use the Brusselator model where

$A \rightarrow X$
$2X + 3Y \rightarrow 3X$
$B + X \rightarrow Y + D$
$X \rightarrow E$

- Clearly D and E have no effect on the dynamics
- Assume A, B are in excess so their concentrations are constant

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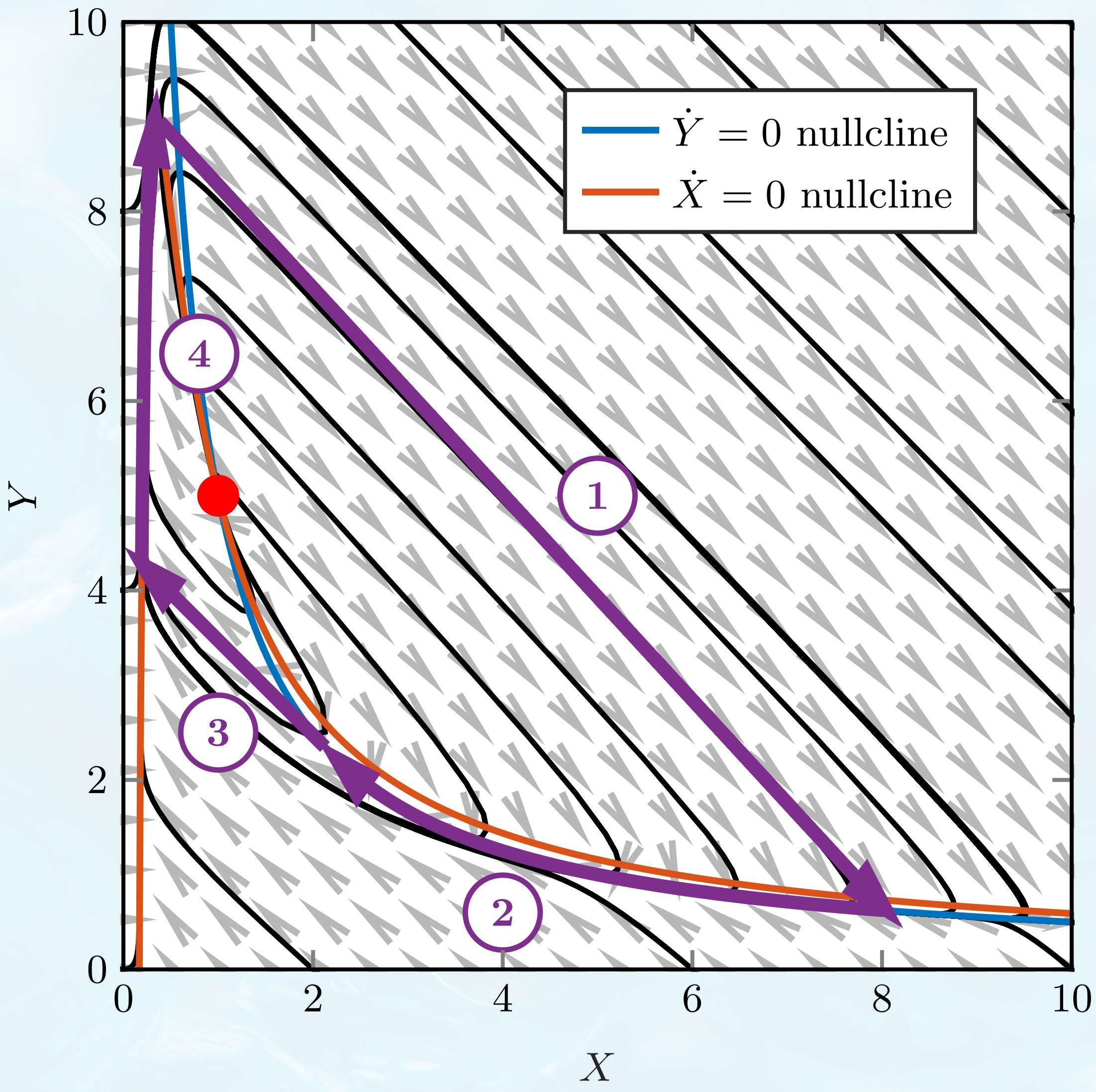
The BZ reaction

$$\frac{\mathrm{d}X}{\mathrm{d}t} = A + X^2Y - (1+B)X$$
$$\frac{\mathrm{d}Y}{\mathrm{d}t} = BX - X^2Y$$

$$(X^*,\, Y^*) = (A,\, B/A)$$

- The time spent on the limit cycle can be approximated: dynamics are fast in regions 1-3 until we collapse onto the X nullcline

$$T \approx \int_0^{Y_{\max}} \frac{dY}{\dot{Y}} \approx \frac{(1+B)^2}{4A^2}$$



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Coupling with gel dynamics

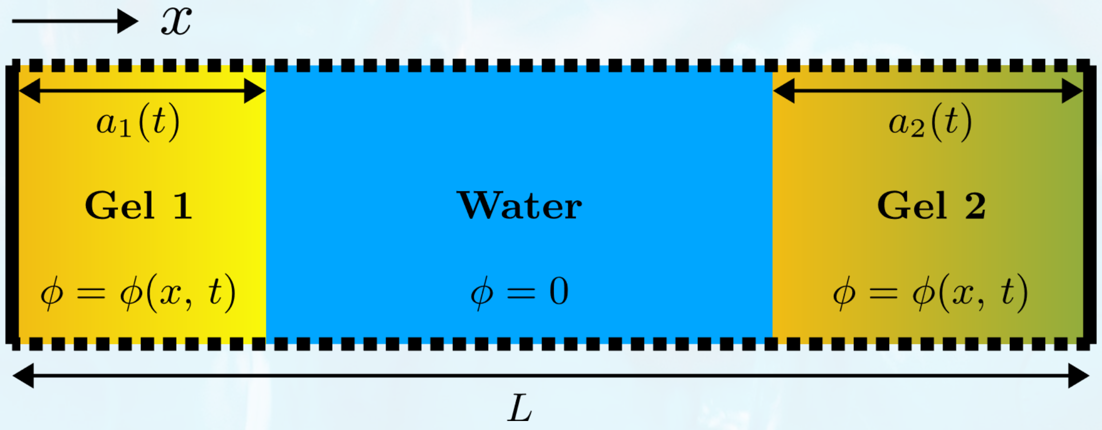
- Oscillating chemical reactions have been coupled with chemo-responsive gels to create periodic shape changes in the modelling of heart tissues (Yoshida, *Biophysics Nagoya-Shi* 2012), the creation of crawling microbots (Mao *et al. Extreme Mech Lett* 2020) and the development of soft machines (Nava-Medina *et al. Adv Mater Technol* 2021)

- In general, a catalyst molecule is chemically-bonded to the gel scaffold so that reaction rates increase in a dry gel and decrease in a swollen one

- The polymer will lose its affinity for water when the concentration of Y exceeds a set threshold

$$\phi_0(Y) = \begin{cases} \phi_{00} & Y \leq Y_C \\ \phi_{0\infty} & Y > Y_C \end{cases}$$

A model system



Swelling-dependent catalysis

$$\frac{\partial X}{\partial t} + q\frac{\partial X}{\partial x} = r(\phi)\left[A + X^2Y - (1+B)X\right] + \mathcal{D}\frac{\partial^2 X}{\partial x^2}$$

$$\frac{\partial Y}{\partial t} + q\frac{\partial Y}{\partial x} = r(\phi)\left[BX - X^2Y\right] + \mathcal{D}\frac{\partial^2 Y}{\partial x^2}$$

Pumping of interstitial fluid in gel
Equal to zero outside of gel, given by fluid fluxes within the gel (water flow from swollen to dried regions)

Chemical diffusion
Faster in water than impermeable gel

Couple this with familiar gel dynamics

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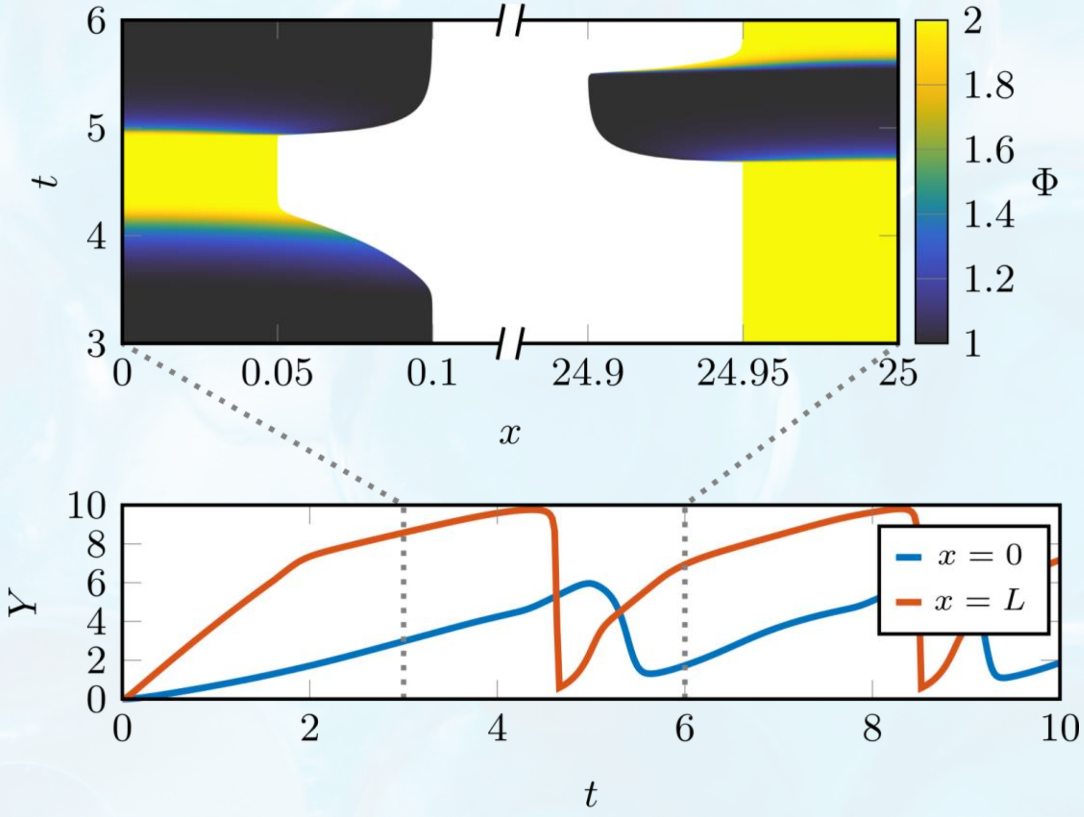
A model system



Parameters: *A=1*, *B=5*, *L=25*, $a_0 = 0.1$, reaction rate *5* times faster in right-hand gel, scaled diffusivities are *1000* in water, *0.2* in gel. $Y_C = 5$ and the equilibrium polymer fraction doubles above the critical threshold. The Damköhler number is *1*.

- This system can be modelled numerically, taking into account:
    - Transport of water and solute into and out of gels as they deswell and swell
    - Molecular diffusion of chemical species
    - The BZ reaction in each gel
    - Changes to reaction rates due to swelling and deswelling

- Lots of timescales here, introduce

Rate constant for reaction

Gel permeability

$$Da_I = \frac{k_r \mu_l a_0^2}{k \Pi_0} \lesssim 1$$

i.e. assume reconfiguration is fast!

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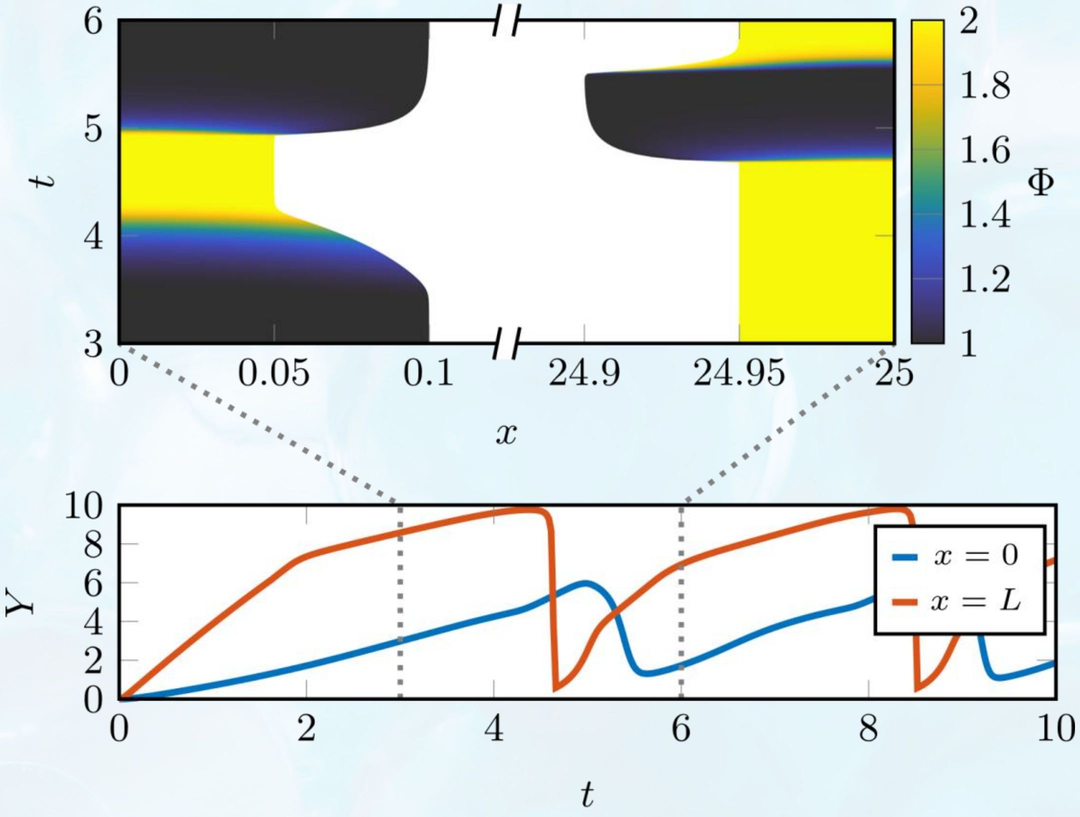
Coupled oscillator model



Parameters: *A=1*, *B=5*, *L=25*, $a_0 = 0.1$, reaction rate *5* times faster in right-hand gel, scaled diffusivities are *1000* in water, *0.2* in gel. $Y_C = 5$ and the equilibrium polymer fraction doubles above the critical threshold. The Damköhler number is *1*.

We can reduce these PDEs to a simpler coupled oscillator model, assuming:

- **Diffusion is fast** in gels, so chemical concentration is approximately constant within
- **Diffusion is fast** in water, so there are linear profiles here

$$X = X_1 + \frac{X_2 - X_1}{L - a_1 - a_2}(x - a_1)$$

$$Y = Y_1 + \frac{Y_2 - Y_1}{L - a_1 - a_2}(x - a_1)$$

- **Neglect osmotic pumping**
- **Diffusion is much faster in water than in gel** so the diffusive flux in the water approximates the flow of chemical into or out of a gel.

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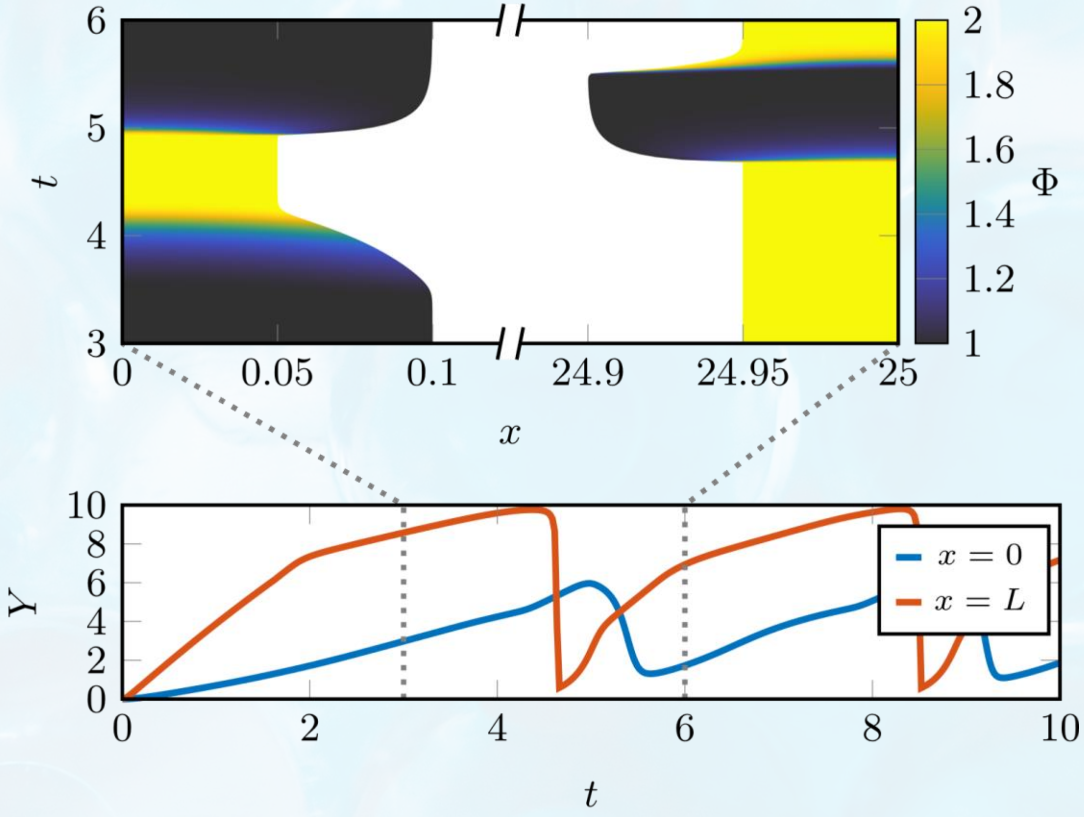
UCL Mathematical Biology Meeting 30/10/24

Coupled oscillator model



Parameters: *A=1*, *B=5*, *L=25*, a_0 = *0.1*, reaction rate *5* times faster in right-hand gel, scaled diffusivities are *1000* in water, *0.2* in gel. Y_C = *5* and the equilibrium polymer fraction doubles above the critical threshold. The Damköhler number is *1*.

- **Diffusion is fast** in gel and water
- **Neglect osmotic pumping**
- **Diffusion is much faster in water than in gel**

- **Damköhler number is small** so gels instantaneously reach equilibrium

$$\frac{\mathrm{d}X_1}{\mathrm{d}t} = r(\phi_0(Y_1))R_X(X_1,\, Y_1) + \frac{Qa_0}{a_1}(X_2 - X_1),$$
$$\frac{\mathrm{d}X_2}{\mathrm{d}t} = r(\phi_0(Y_2))R_X(X_2,\, Y_2) - \frac{Qa_0}{a_2}(X_2 - X_1),$$
$$\frac{\mathrm{d}Y_1}{\mathrm{d}t} = r(\phi_0(Y_1))R_Y(X_1,\, Y_1) + \frac{Qa_0}{a_1}(Y_2 - Y_1),$$
$$\frac{\mathrm{d}X_2}{\mathrm{d}t} = r(\phi_0(Y_2))R_Y(X_2,\, Y_2) - \frac{Qa_0}{a_2}(Y_2 - Y_1).$$

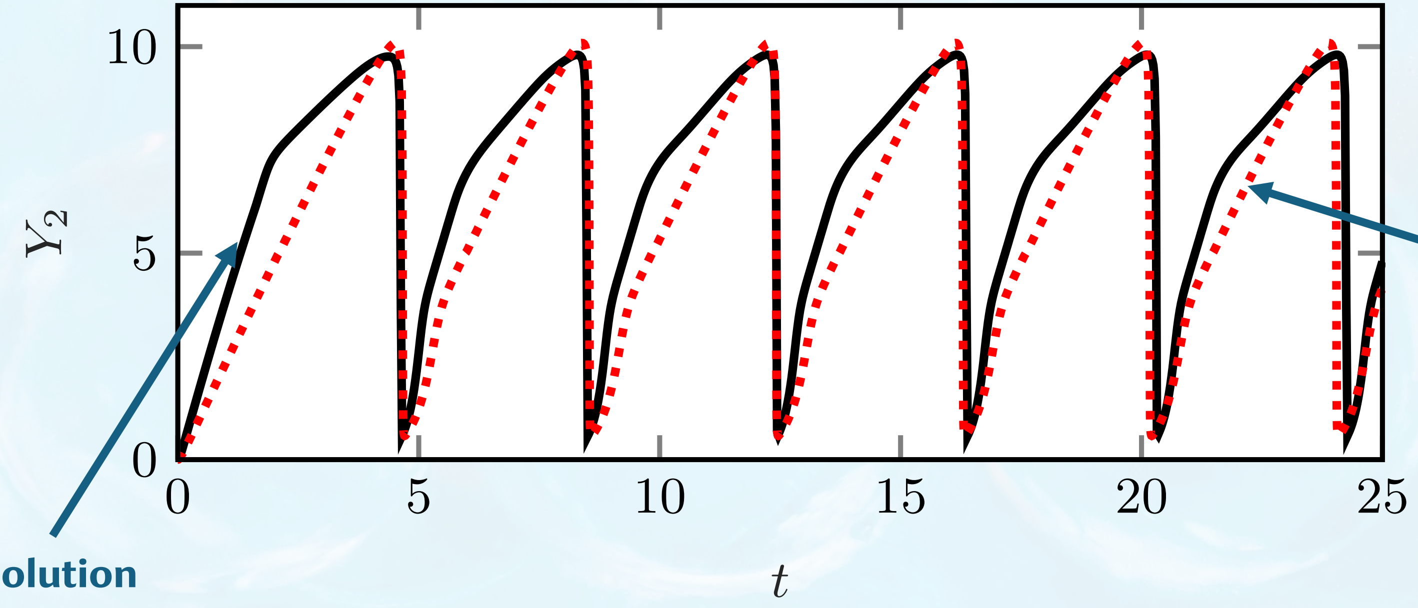
Reaction terms

Coupling strength
Q = D_{water} / $a_0 L$

where e.g. $a_1/a_0 = \phi_{00}/\phi_0(Y_1)$

Coupled oscillator model

Parameters: *same as before*



Full numerical solution
Y evaluated at *x*=*L*

Coupled oscillators

$$
\begin{aligned}
\frac{\mathrm{d}X_1}{\mathrm{d}t} &= r(\phi_0(Y_1))R_X(X_1, Y_1) + \frac{Qa_0}{a_1}(X_2 - X_1),\\
\frac{\mathrm{d}X_2}{\mathrm{d}t} &= r(\phi_0(Y_2))R_X(X_2, Y_2) - \frac{Qa_0}{a_2}(X_2 - X_1),\\
\frac{\mathrm{d}Y_1}{\mathrm{d}t} &= r(\phi_0(Y_1))R_Y(X_1, Y_1) + \frac{Qa_0}{a_1}(Y_2 - Y_1),\\
\frac{\mathrm{d}X_2}{\mathrm{d}t} &= r(\phi_0(Y_2))R_Y(X_2, Y_2) - \frac{Qa_0}{a_2}(Y_2 - Y_1).
\end{aligned}
$$

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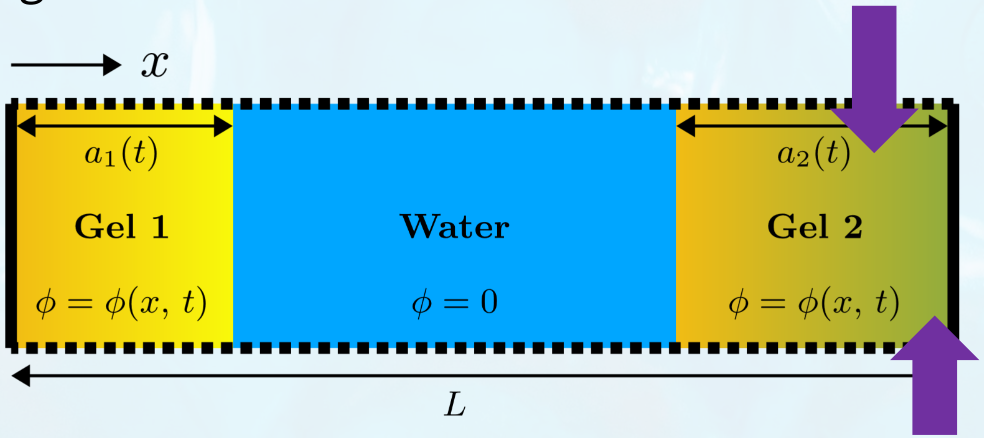
Gels squeal under pressure

- In the first example, we arbitrarily set the reaction rate faster in the second gel than in the first – this gave limit cycles of different periods on each side

- The polymer fraction varies under changes in chemical concentration, but it can also be varied by applying a strain to one gel



Applying a fixed strain *E(t)*
This allows us another control on the polymer fraction and therefore on the reaction rate here

For a stiff gel, $\Phi \approx (1+E)^2$

- For stronger coupling (Q large), there is a penalty to a nonzero value of X_2-X_1 or Y_2-Y_1 – therefore, if the two gels are especially close or the diffusion of chemical species is fast through the gap, there is synchronisation in their periods

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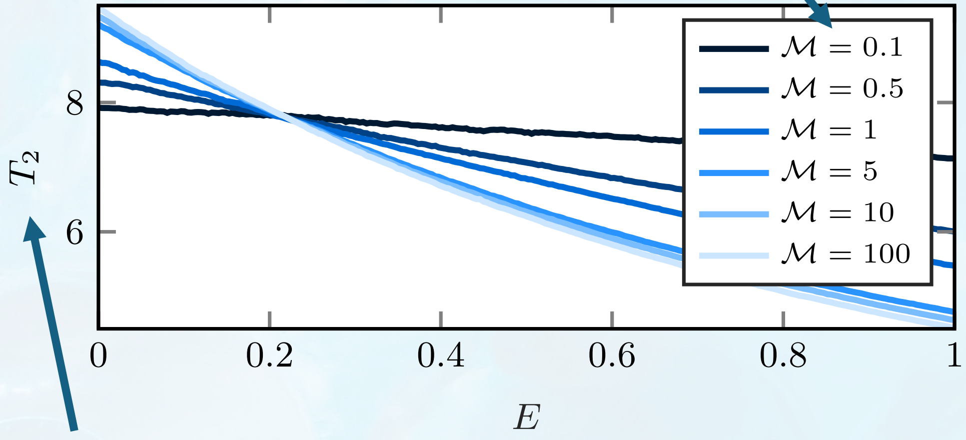
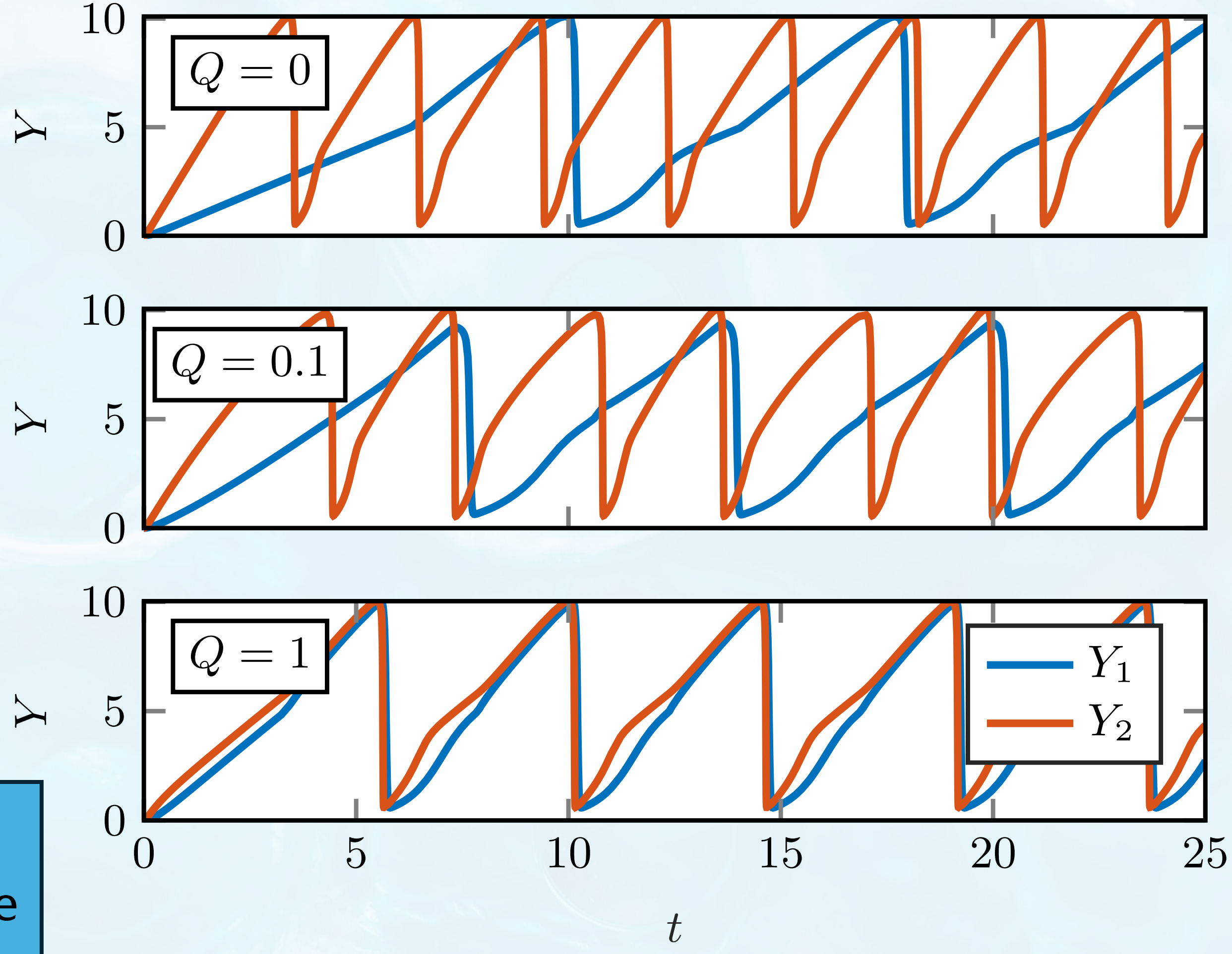
Gels squeal under pressure

Parameter measuring stiffness of gel



Time period for second oscillator

Parameters: *same as before with E = 1 on second gel*



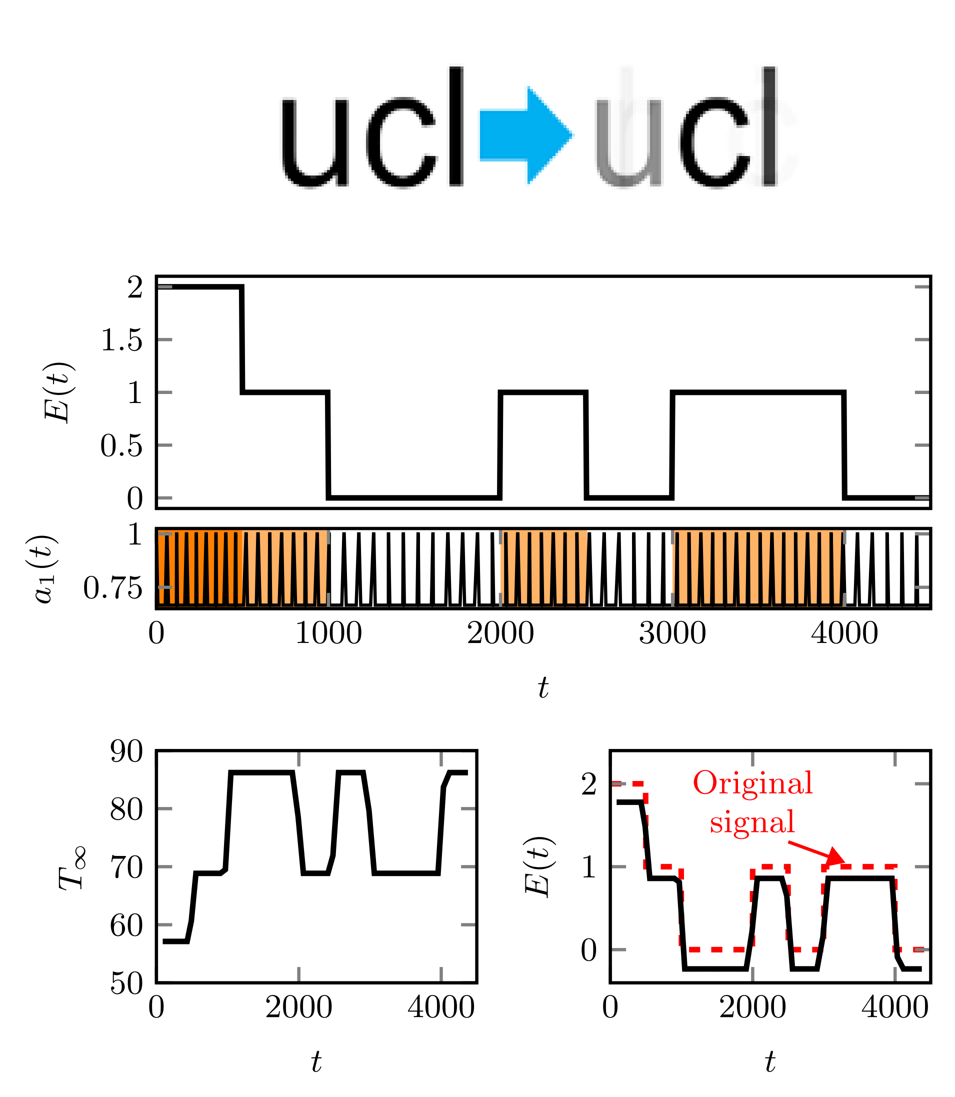
More compression, higher polymer fraction, higher rate of reaction

Where does this leave us?

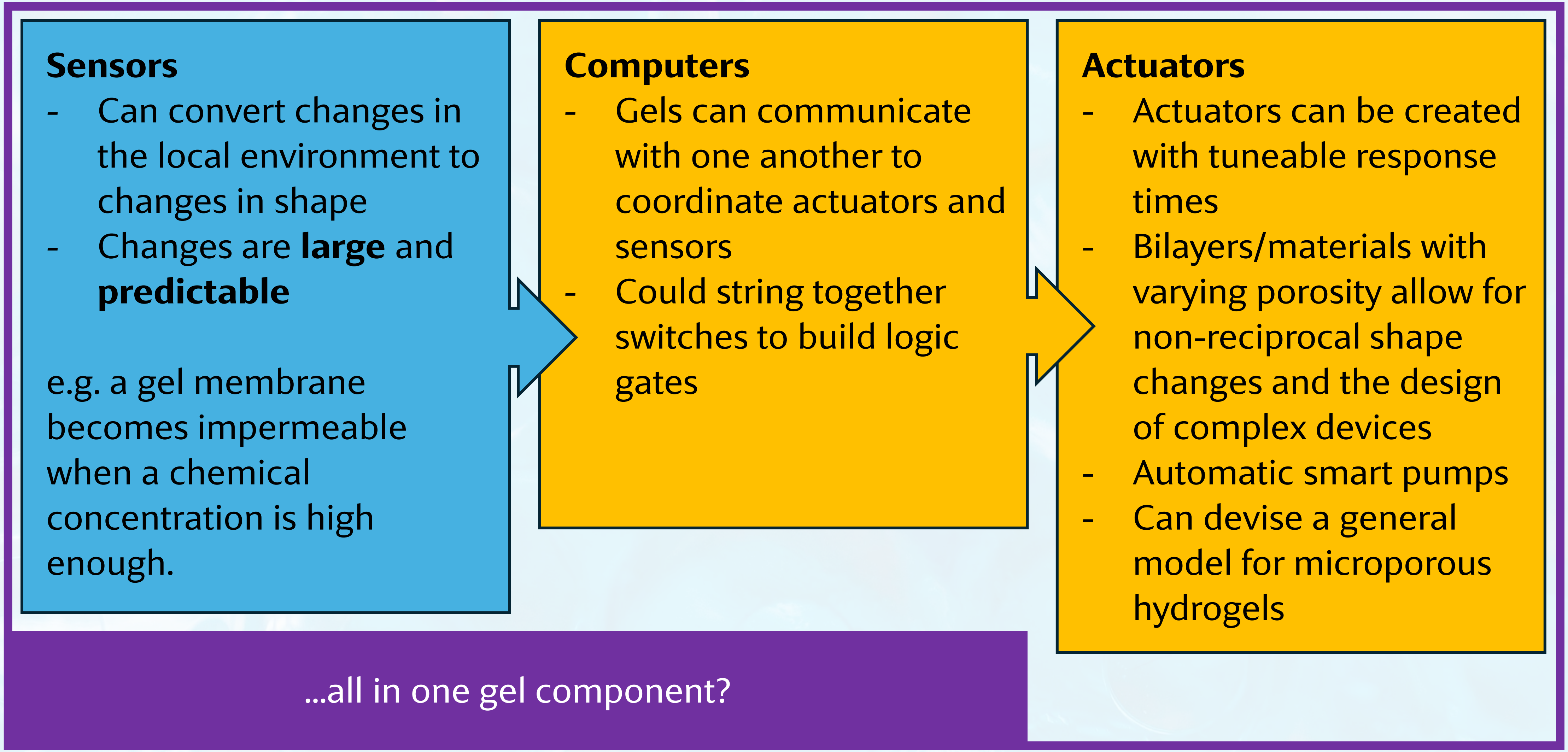
- We can modulate the compression on the second gel and measure the time period of the oscillations of the first gel. In the limit of strong coupling

$$T_1 \approx T_2 \approx \frac{(B+1)^2}{2(r_1+r_2)A^2}$$

- Seeing as the reaction rate of the first gel is known, this allows us to measure the reaction rate of the second gel and therefore find the compression that is being applied, allowing for communication



Next steps



Sensors

- Can convert changes in the local environment to changes in shape
- Changes are **large** and **predictable**

e.g. a gel membrane becomes impermeable when a chemical concentration is high enough.

Computers

- Gels can communicate with one another to coordinate actuators and sensors
- Could string together switches to build logic gates

Actuators

- Actuators can be created with tuneable response times
- Bilayers/materials with varying porosity allow for non-reciprocal shape changes and the design of complex devices
- Automatic smart pumps
- Can devise a general model for microporous hydrogels

...all in one gel component?

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Next steps

Even though hydrogels have been modelled for decades, there's still a need for **simple**, **macroscopic** models that capture the key phenomena without recourse to microscopic modelling: these can both follow experimental advances (tubes) or inform new implementations (communicating gels)

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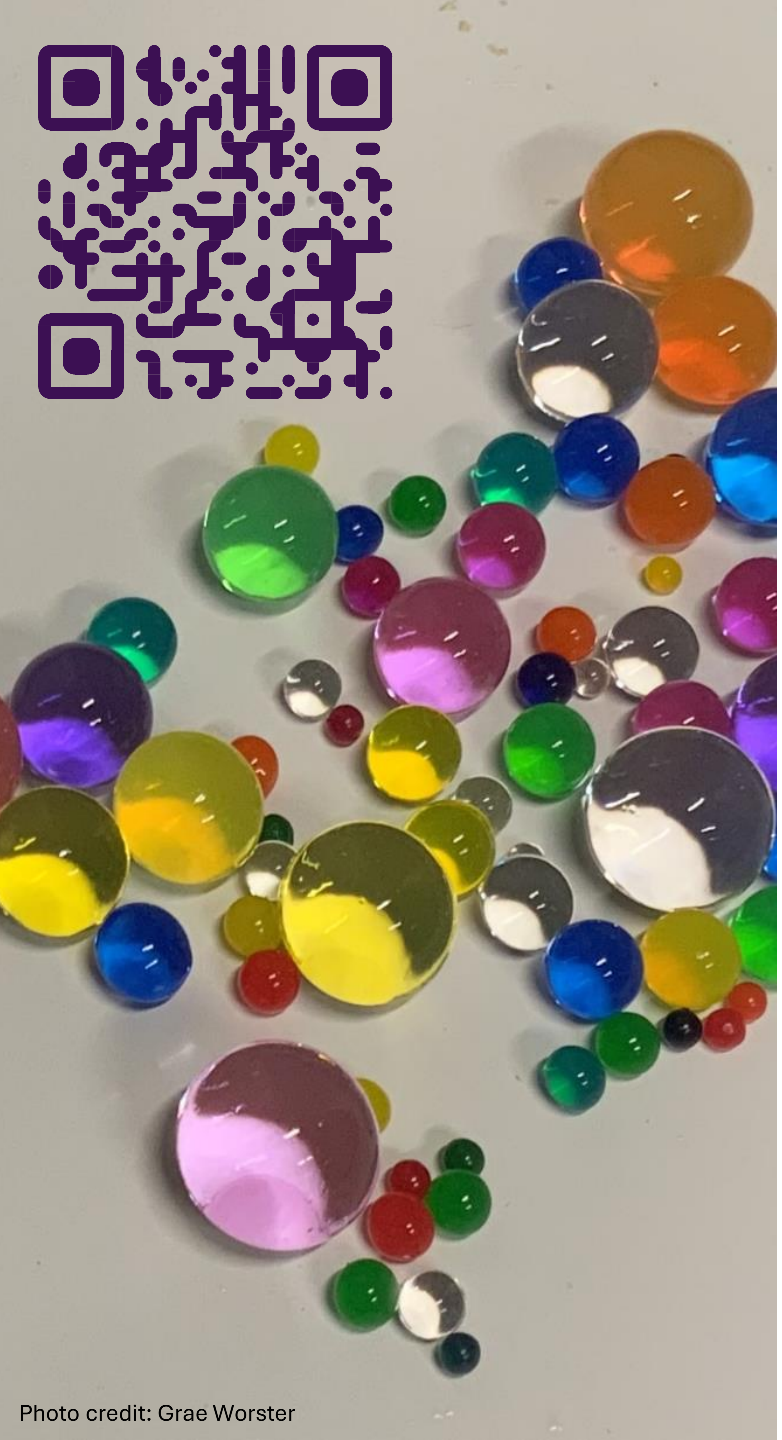

Photo credit: Grae Worster

Modelling hydrogels: building networks in the Mathematical Sciences

Mathematical Interdisciplinary Research at Warwick (MIR@W) Day

Warwick Mathematics Institute, 9th December 2024

Organisers: *Joe Webber and Tom Montenegro-Johnson*

1. Living gels, living with gels: hydrogels in microbiology and medicine

2. At the surface and through the pores: transport and interfacial behaviour

3. Feeling the surroundings: hydrogels as smart materials

Confirmed speakers

- Matthew Butler (UCL)
- Matt Hennessy (Bristol)
- Chris MacMinn (Oxford)
- Philip Pearce (UCL)
- Draga Pihler-Puzović (Manchester)
- Grae Worster (Cambridge)

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