xoxo, gossip gel

oscillating chemical reactions facilitate communication between responsive hydrogels

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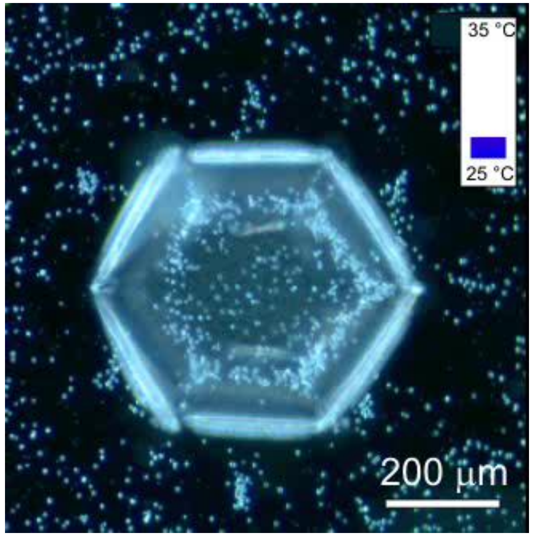
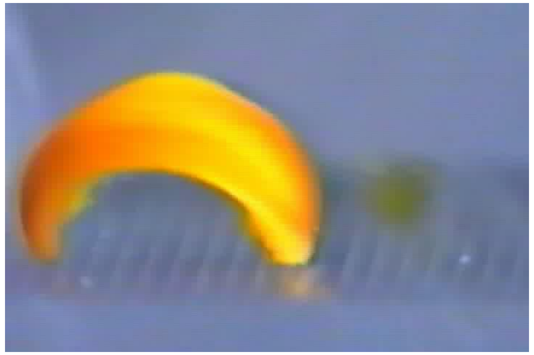
Overview

1. Responsive gels
2. Modelling responsive gels *quickly* and *macroscopically*
3. The BZ oscillating reaction
4. Coupling oscillating reactions with responsive gels
5. Gels + oscillating reaction + imposed strain = profit?

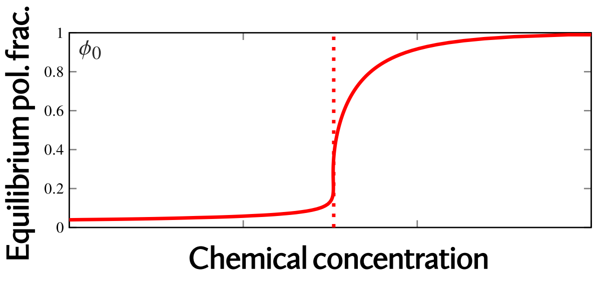




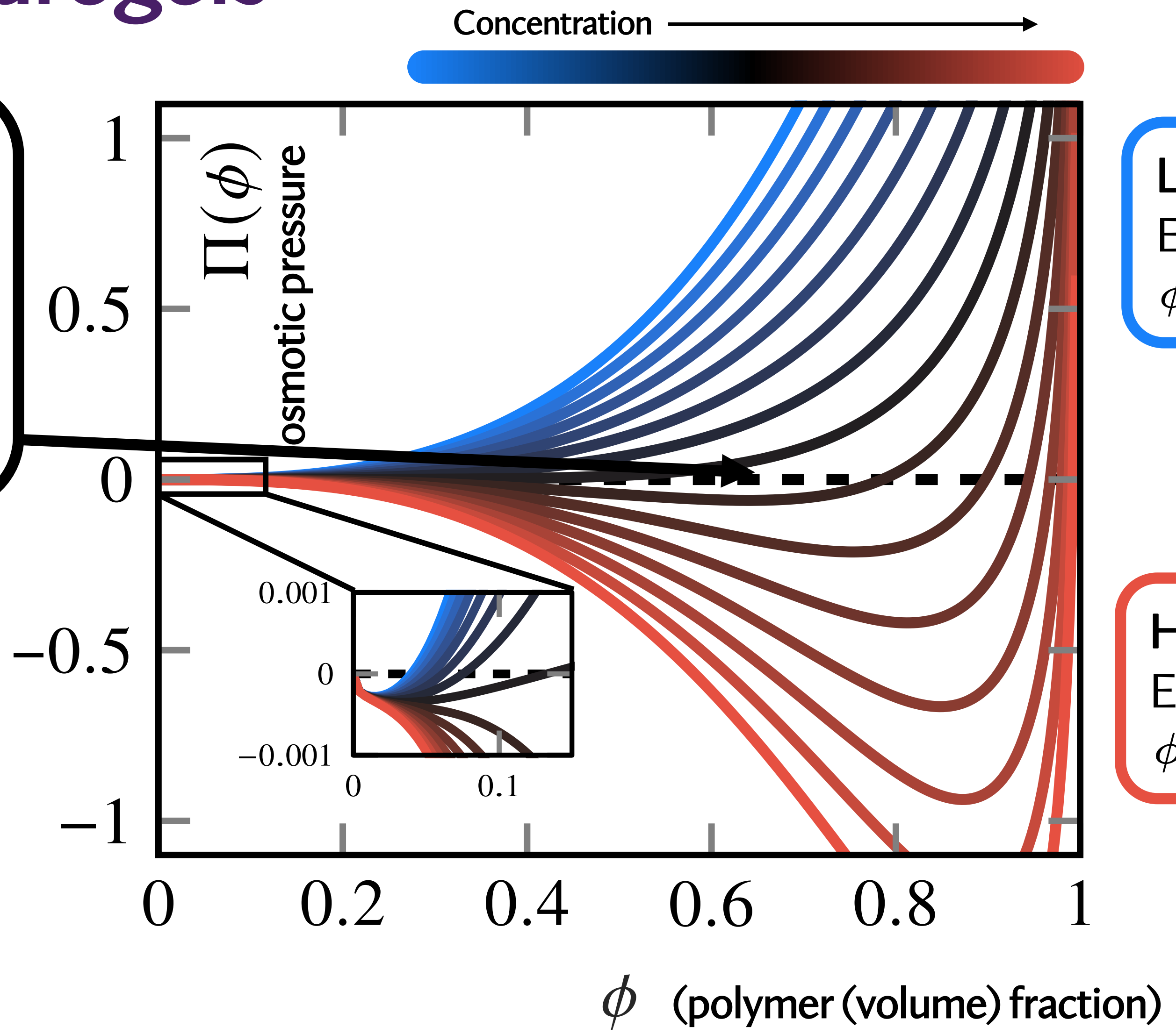
1. **Stoychev *et al.*** Soft Matter 7 (2011)
2. **Maeda *et al.*** Advanced Materials 19 (2007)

Responsive hydrogels

Sharp transition



Equilibrium swelling
The polymer volume fraction where the osmotic pressure is zero



Low concentration
Equilibrium swelling large
$\phi_{00} \approx 5\%$

High concentration
Equilibrium swelling large
$\phi_{0\infty} \approx 95\%$

Responsive hydrogels: modelling

Osmotic components

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

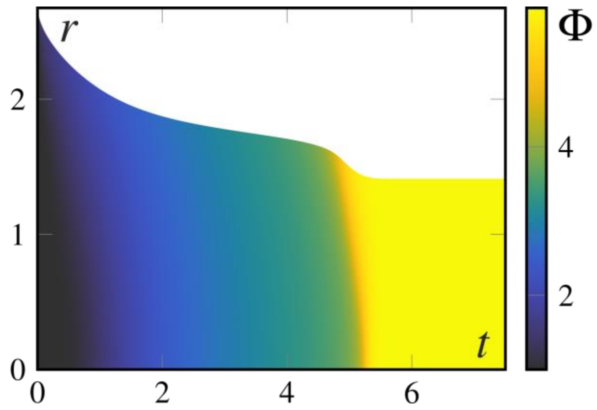
$$\Pi(\phi) = \Pi_0 \frac{\phi - \phi_0(Y)}{\phi_0(Y)}$$

LENS modelling

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

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

Webber & Worster *and* Webber *et al.* (JFM 2023)



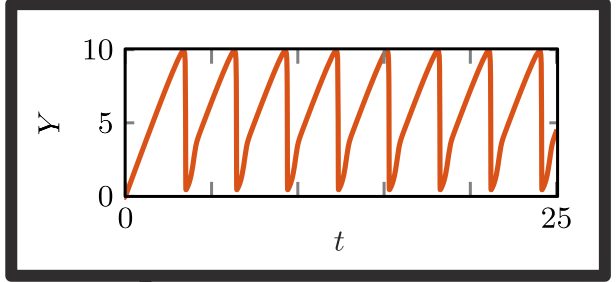
- Any gel described by three material parameters: osmotic pressure (responsivity), shear modulus (nature of response) and permeability (speed of response).
- Response occurs generally slowly by driving water in or out of the polymer scaffold.

Oscillating reactions and oscillating gels

BZ reaction

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

assume A, B are in excess

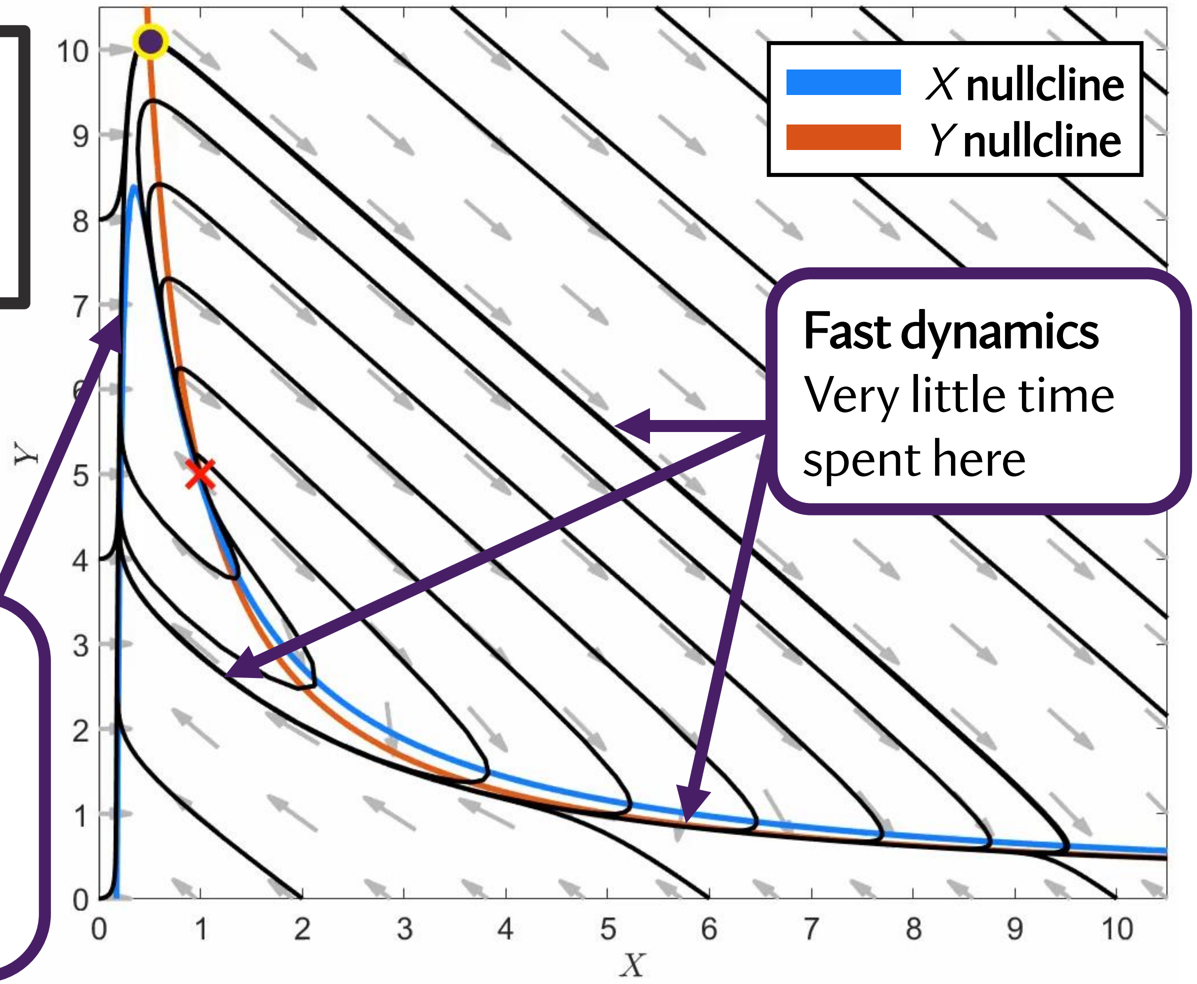


$$\frac{\mathrm{d}X}{\mathrm{d}t} = k\left[A + X^2Y - (1+B)X\right]$$
$$\frac{\mathrm{d}Y}{\mathrm{d}t} = k\left[BX - X^2Y\right]$$

One fixed point at $(X, Y) = (A, B/A)$, unstable provided $B > 1 + A^2$

Slow dynamics
On X nullcline

$$T \approx \frac{(B+1)^2}{4kA^2}$$



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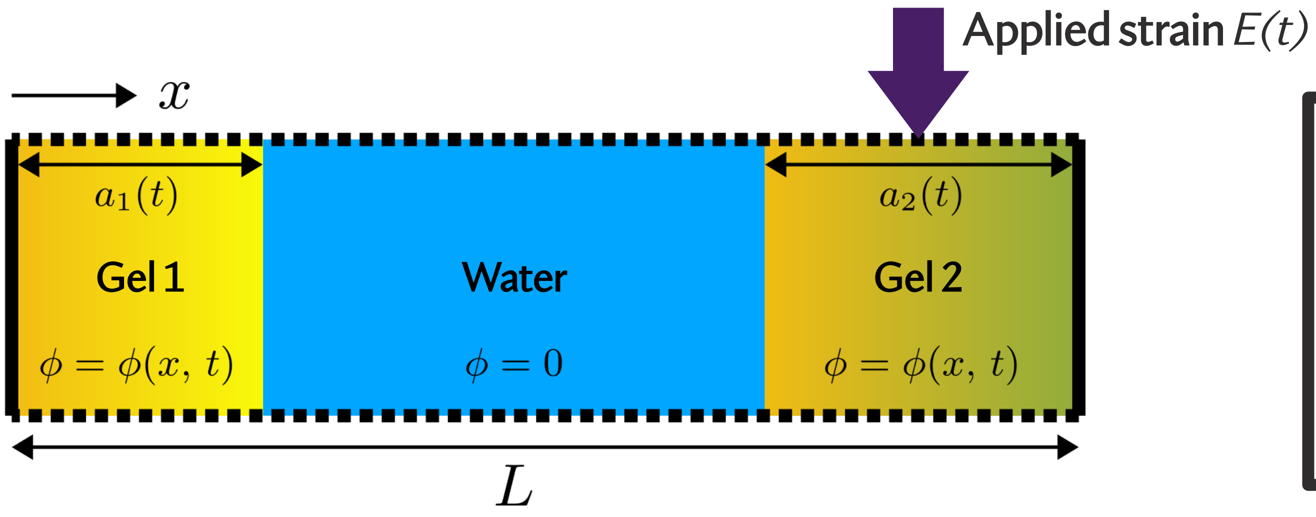
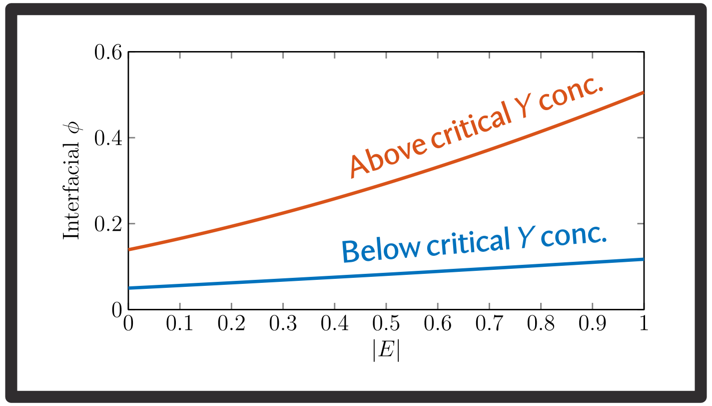
A simple system

Catalyst chemically bound to scaffold
$\uparrow \phi \ \Rightarrow \uparrow \text{catalyst conc.}$





Diffusion on poroelastic timescale

$$\frac{\partial \phi}{\partial t} = \frac{\partial}{\partial x}\left[D(\phi,\, Y)\frac{\partial \phi}{\partial x}\right]$$

$$\phi_{00} a_0 = \int_{\mathrm{Gel}} \phi(x,\, t)\, \mathrm{d}x$$

Mass conservation sets gel thickness

Applying a strain changes the interfacial boundary condition and so deswells gel 2

$$0 = \sigma_{xx} = -P + 2\mu_s \epsilon_{xx} = -P - 2\mu_s \epsilon_{zz} = -\Pi + 2\mu_s \left[1 - (\phi/\phi_{00})^{1/3} - E(t)\right]$$

No stress at gel-fluid boundary

Pervadic pressure continuous: $P = p + \Pi = \Pi$

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Transport of chemical species

Reaction (only in gel)

$k\left[A + X^2Y - (1+B)X\right]$ $(c{=}X)$

$k\left[BX - X^2Y\right]$ $(c{=}Y)$

Advection with flow

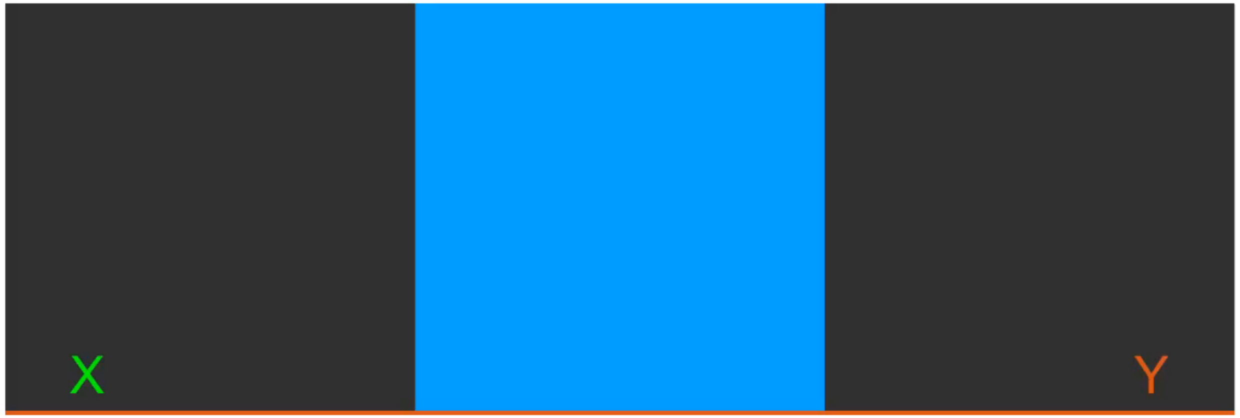
Assume no flow in water, Darcy flow in gel

$$u = -\frac{k(\phi)}{\mu_l}\frac{\partial p}{\partial x} = -\frac{D(\phi,Y)}{\phi}\frac{\partial \phi}{\partial x}$$

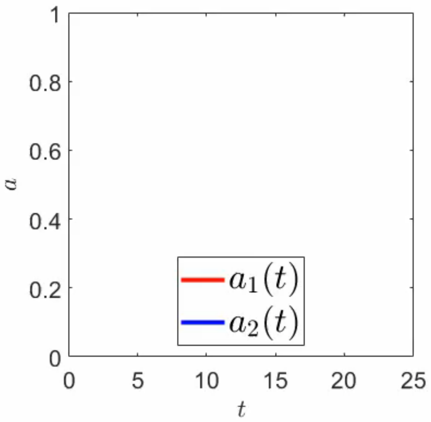
$$\frac{\partial c}{\partial t} + u\frac{\partial c}{\partial x} = \mathcal{R} + D_c\frac{\partial^2 c}{\partial x^2}$$

Diffusion

Different coefficient in water and gel



Reaction rate constant 5 times higher than in left-hand gel



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Coupled oscillator models

$t_{\text{diff, water}} \ll t_{\text{pore}} = t_{\text{diff, gel}} \ll t_{\text{react}}$

A1: Diffusion is fast in the water $\partial^2 c/\partial x^2 \approx 0 \Rightarrow c = c_1 + \dfrac{c_2 - c_1}{L - a_1(t) - a_2(t)}[x - a_1(t)]$

A2: Gel response is rapid (*Da < 1*) $|q(\partial c/\partial x)| \ll 1$ and $\phi(x,\, t) \equiv \phi_0(Y(t))$ so $a_i(t) = \phi_{00} a_0/\phi$

A3: Diffusion is fast in the gel $c \equiv c_1,\ c_2$ in each gel, respectively

A4: Reaction rates are proportional to polymer fraction $k = K_i/a_i(t)$ (where K_i depends on compression)

$$\frac{\partial X}{\partial t} + u(x,\, t)\frac{\partial X}{\partial x} = k(x,\, t)\left[A + X^2 Y - (1+B)X\right] + D_c(x,\, t)\frac{\partial^2 X}{\partial x^2}$$

$$\frac{\partial Y}{\partial t} + u(x,\, t)\frac{\partial Y}{\partial x} = k(x,\, t)\left[BX - X^2 Y\right] + D_c(x,\, t)\frac{\partial^2 Y}{\partial x^2}$$

$\Rightarrow$

$$\frac{\mathrm{d}X_1}{\mathrm{d}t} = \frac{K_1}{a_1(t)}\left[A + X_1^2 Y_1 - (1+B)X_1\right] + \frac{\mathcal{Q}}{a_1(t)}(X_2 - X_1)$$

$$\frac{\mathrm{d}X_2}{\mathrm{d}t} = \frac{K_2}{a_2(t)}\left[A + X_2^2 Y_2 - (1+B)X_2\right] + \frac{\mathcal{Q}}{a_1(t)}(X_1 - X_2)$$

$$\frac{\mathrm{d}Y_1}{\mathrm{d}t} = \frac{K_1}{a_1(t)}\left[BX_1 - X_1^2 Y_1\right] + \frac{\mathcal{Q}}{a_1(t)}(Y_2 - Y_1)$$

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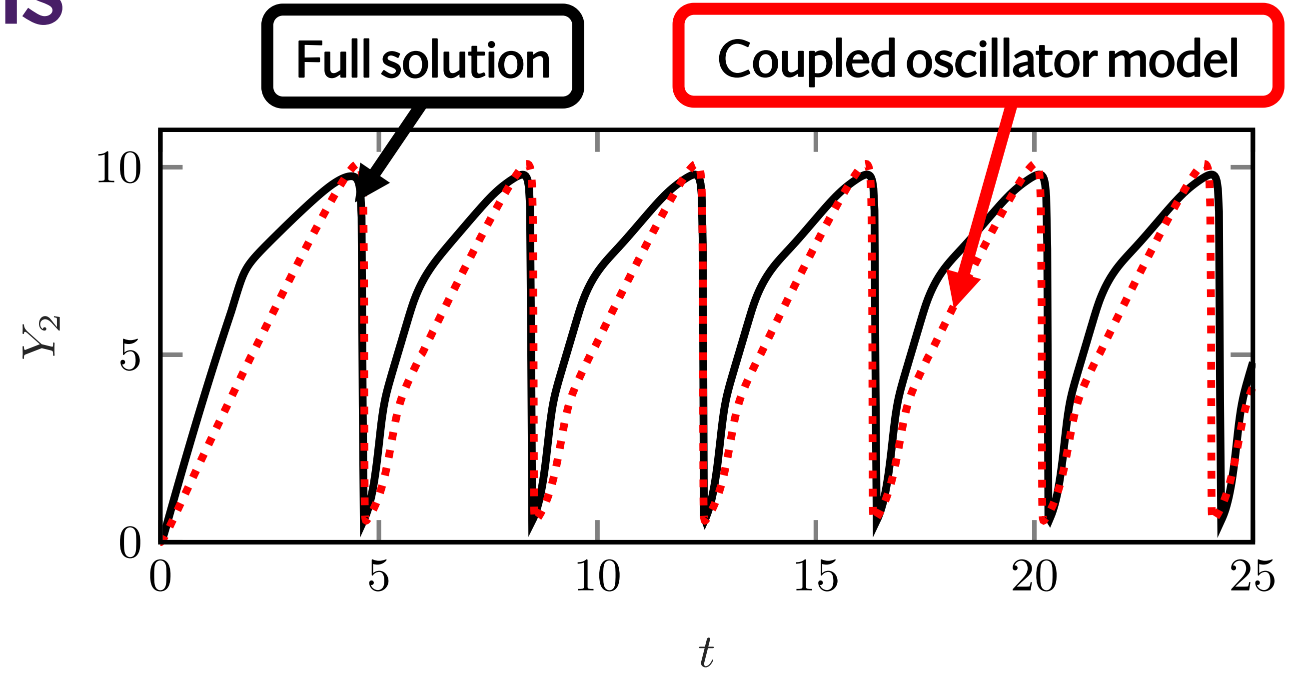


$$a_i(t) = \begin{cases} a_0 & Y \leq Y_C \\ (\phi_{00}/\phi_{0\infty})a_0 & Y > Y_C \end{cases}$$

$$\mathcal{Q} = \frac{D_c^{\mathrm{water}}}{L}$$ is the coupling strength

Note strong coupling implies $X_1=X_2$, $Y_1=Y_2$ and $a_1=a_2$ - add equations pairwise:

$$\frac{\mathrm{d}X}{\mathrm{d}t} = \frac{K_1+K_2}{2a(t)}\left[A + X^2 Y - (1+B)X\right]$$

$$\frac{\mathrm{d}Y}{\mathrm{d}t} = \frac{K_1+K_2}{2a(t)}\left[BX - X^2 Y\right]$$

Coupled oscillator models

$$\frac{\mathrm{d}X}{\mathrm{d}t} = \frac{K_1 + K_2}{2a(t)}\left[A + X^2Y - (1+B)X\right]$$

$$\frac{\mathrm{d}Y}{\mathrm{d}t} = \frac{K_1 + K_2}{2a(t)}\left[BX - X^2Y\right]$$

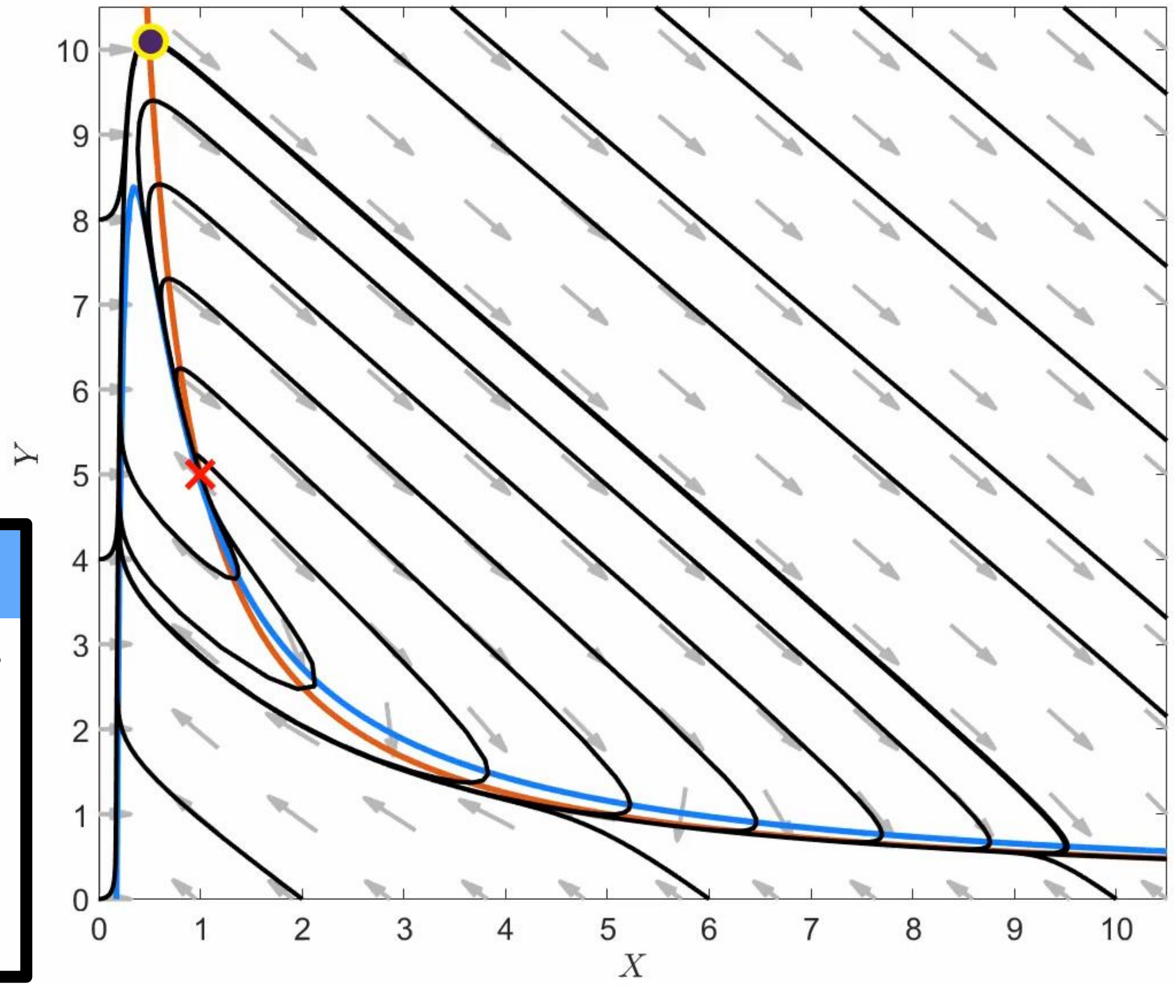
Compute period by integrating to find residence time on slow region of limit cycle

$$T_{1,\,2} \approx \frac{\phi_{00}a_0}{\phi_{0\infty}}\frac{(B+1)^2}{2(K_1+K_2)A^2}$$

Assume gels are shrunken at all times in the slow region

Key result

Oscillation period of gel 1 can tell us K_2, **and thus how hard we are squeezing gel 2!**



Gossip gels?

Take an input signal and convert it to an applied strain on gel 2

apsdfd → 1 16 19 4 6 4

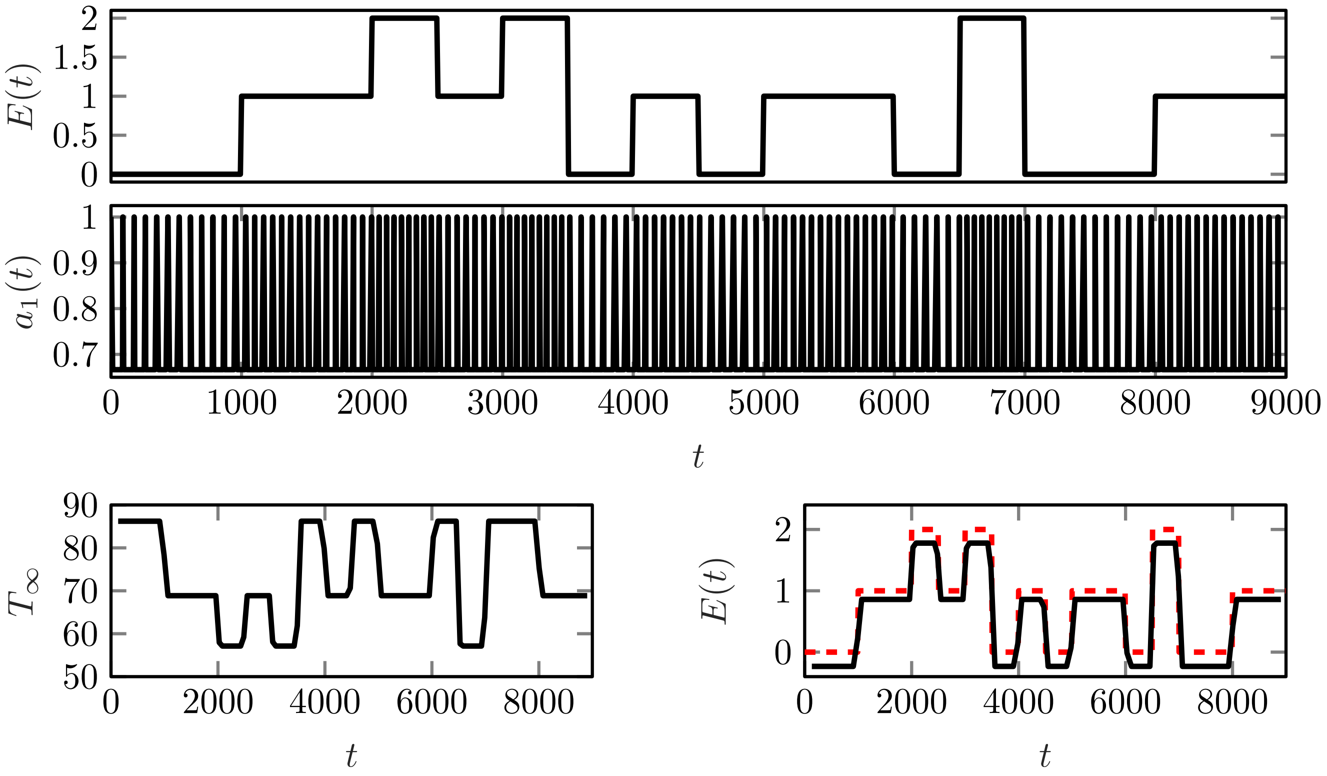
↓

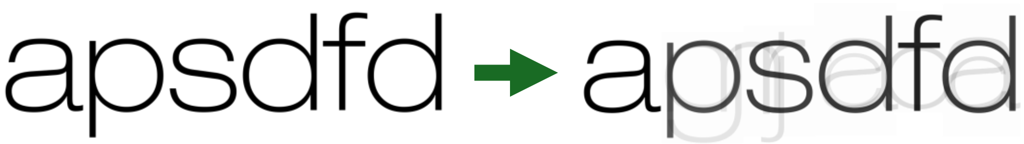
001 121 201 011 020 011

$$E = 0.1 + 0.25 b_i$$

Take $K_1 = 1$ and $K_2 = (1+E)^2$ (for a stiff gel). Measure T for gel 1, then

$$E \approx -1 + \sqrt{\frac{\phi_{00} a_0}{\phi_{0\infty}} \frac{(B+1)^2}{2A^2 T_1} - 1}$$





With thanks to

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