Modelling hydrogels: building networks in the Mathematical Sciences

Mathematical Interdisciplinary Research at Warwick (MIR@W) Day

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Deswelling response to temperature changes

building macroscopic models for thermo-responsive gels

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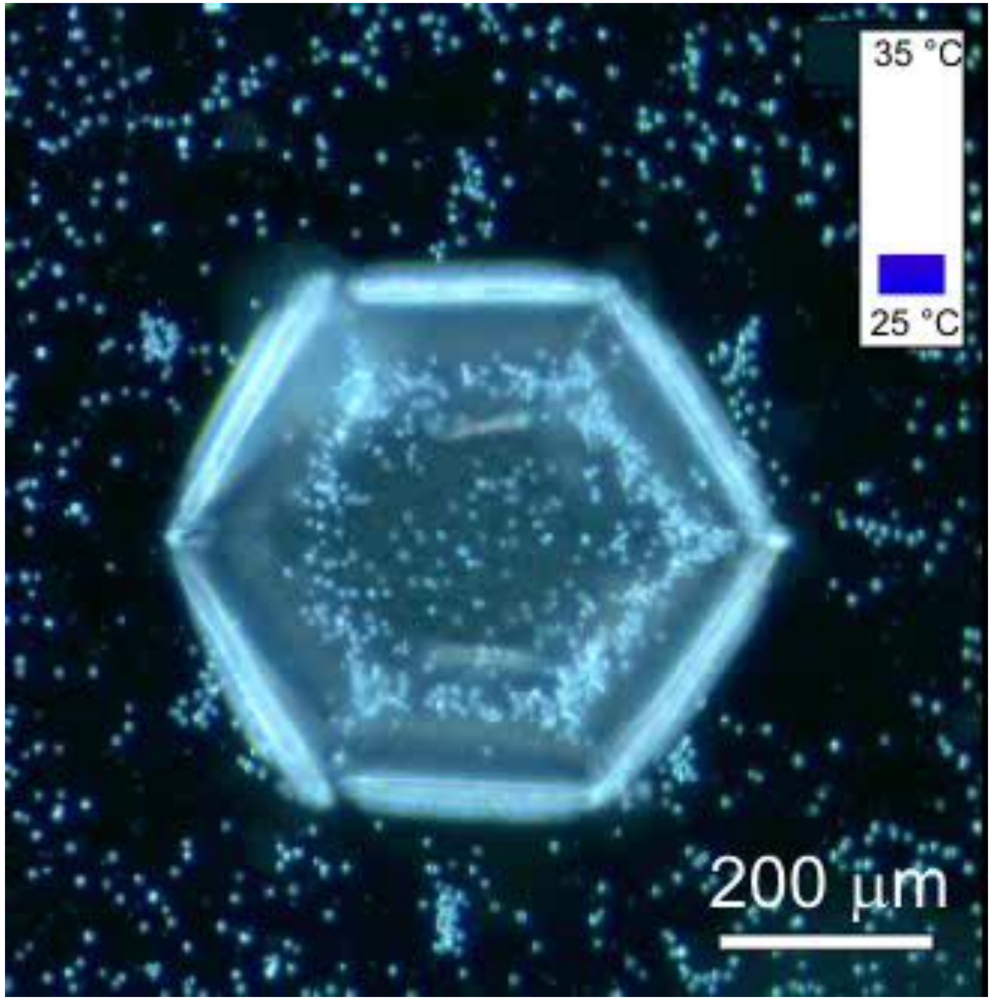
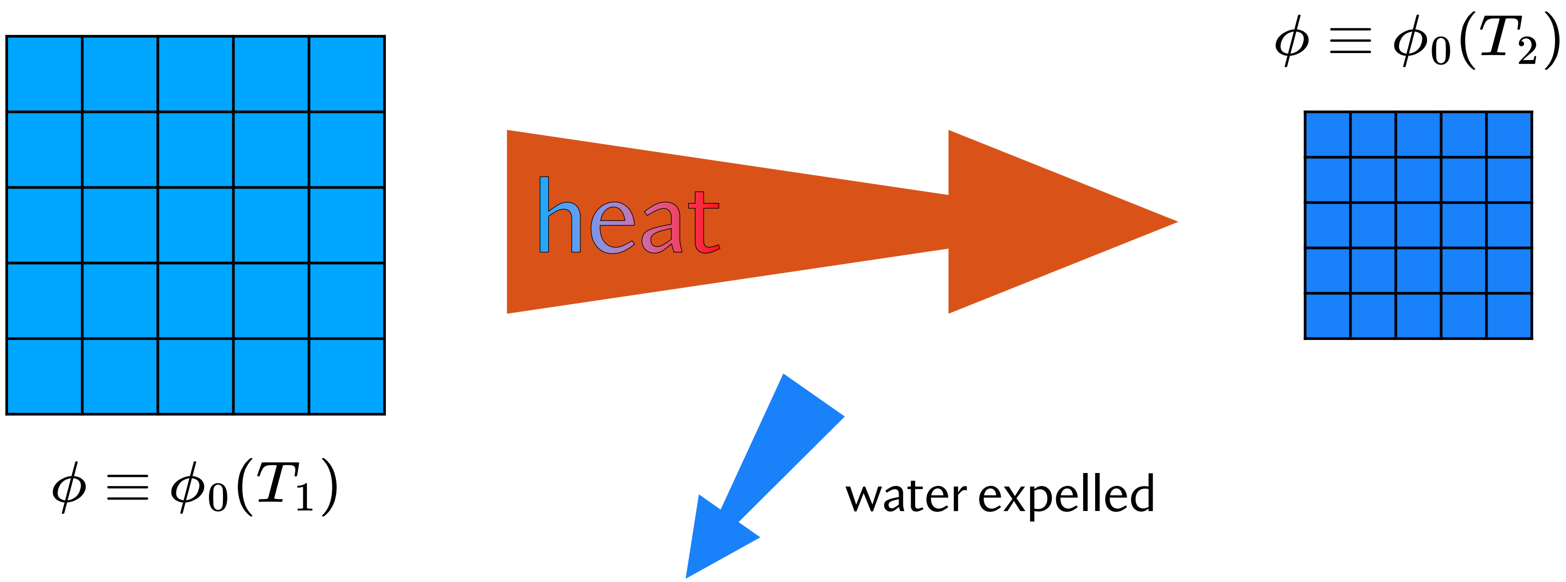


Stoychev *et al.* Soft Matter 7 (2011)

Thermo-responsive hydrogels

ϕ **Polymer (volume) fraction** (1-10% when 'swollen')

Equilibrium polymer fraction = the degree of swelling reached by a gel placed in water, free to swell, in the absence of mechanical constraints



- Takes some time – water diffusion is **slow**
- Qualitatively, looks like there's a single swollen state and a single dry state either side of a **lower critical solution temperature (LCST)** $T = T_C$

...most of the time, anyway, if you ignore Afroze, Nies & Berghmans (2000) or Butler & Montenegro-Johnson (2022)

Thermo-responsive hydrogels

ϕ Polymer (volume) fraction
(1-10% when 'swollen')

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

neo-Hookean elasticity — mixing energy

- Affinity for water is encoded by the Flory chi parameter measuring the strength of electrostatic attraction between polymer and water

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

- Can fit the parameters here from observations – somewhat crude and very sensitive to experimental error

Thermo-responsive LENS

$$\mathsf{e}_{ij} = \left[1 - (\phi/\phi_{00})^{1/3}\right]\delta_{ij} + \epsilon_{ij} \quad \Big| \quad |\epsilon_{ij}| \ll 1$$

$$\sigma_{ij} = -p\delta_{ij} + \phi \frac{\partial \mathcal{W}}{\partial \mathsf{F}_{ik}} \mathsf{F}_{jk}$$

Deformation is, at leading order, isotropic, corresponding to swelling or drying.

Gels are characterised by three material parameters dependent on degree of swelling.

see Webber & Worster (2023)

Measure deformation relative to a "swollen" steady state at a temperature well below the LCST, where $\phi = \phi_{00}$

$$\sigma_{ij} = -\left[p + \Pi(\phi)\right]\delta_{ij} + 2\mu_s(\phi)\epsilon_{ij}$$

- p is the pervadic/pore/Darcy pressure of the fluid
- Π is the osmotic pressure
- μ_s is the shear modulus

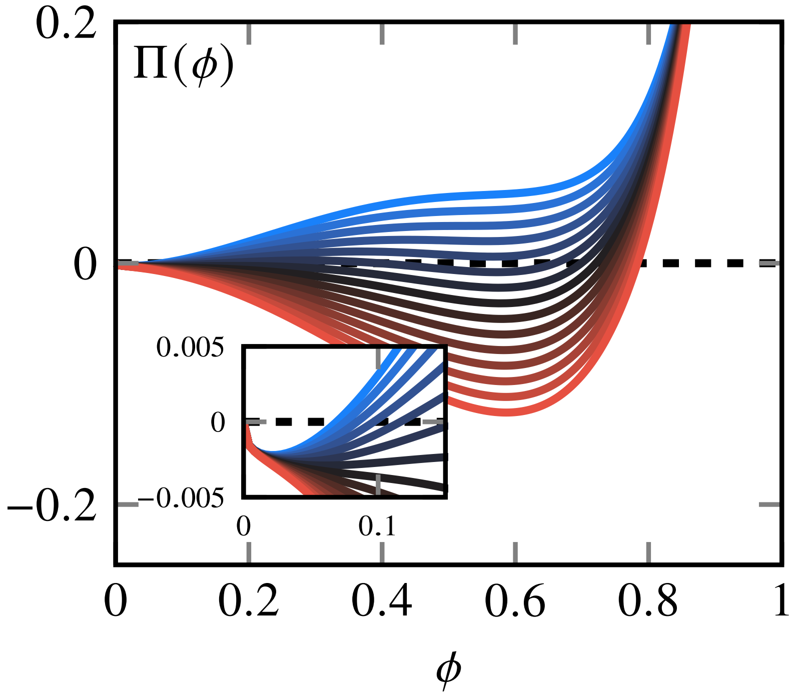
$$\Pi(\phi) = \frac{k_B T}{\Omega_f}\left[\frac{\Omega_f}{\Omega_p}\left(\phi - \phi^{1/3}\right) - \phi - \log(1-\phi) - \phi^2\chi + \phi^2(1-\phi)\frac{\partial \chi}{\partial \phi}\right]$$

$$\mu_s(\phi) = \frac{k_B T \phi_{00}^{1/3}}{\Omega_p}$$

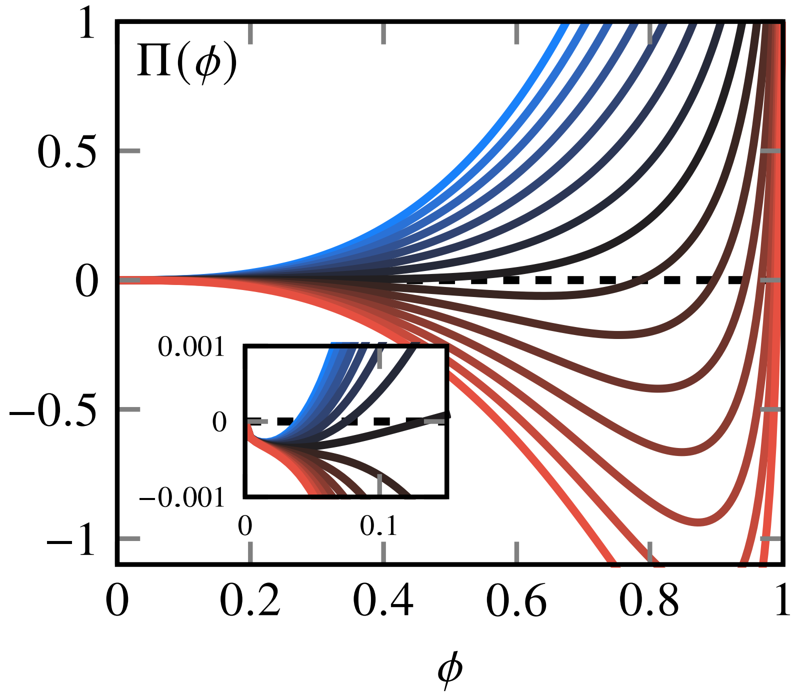
Osmotic pressures

$$\sigma_{ij} = -\left[p + \Pi(\phi)\right]\delta_{ij} + 2\mu_s(\phi)\epsilon_{ij}$$

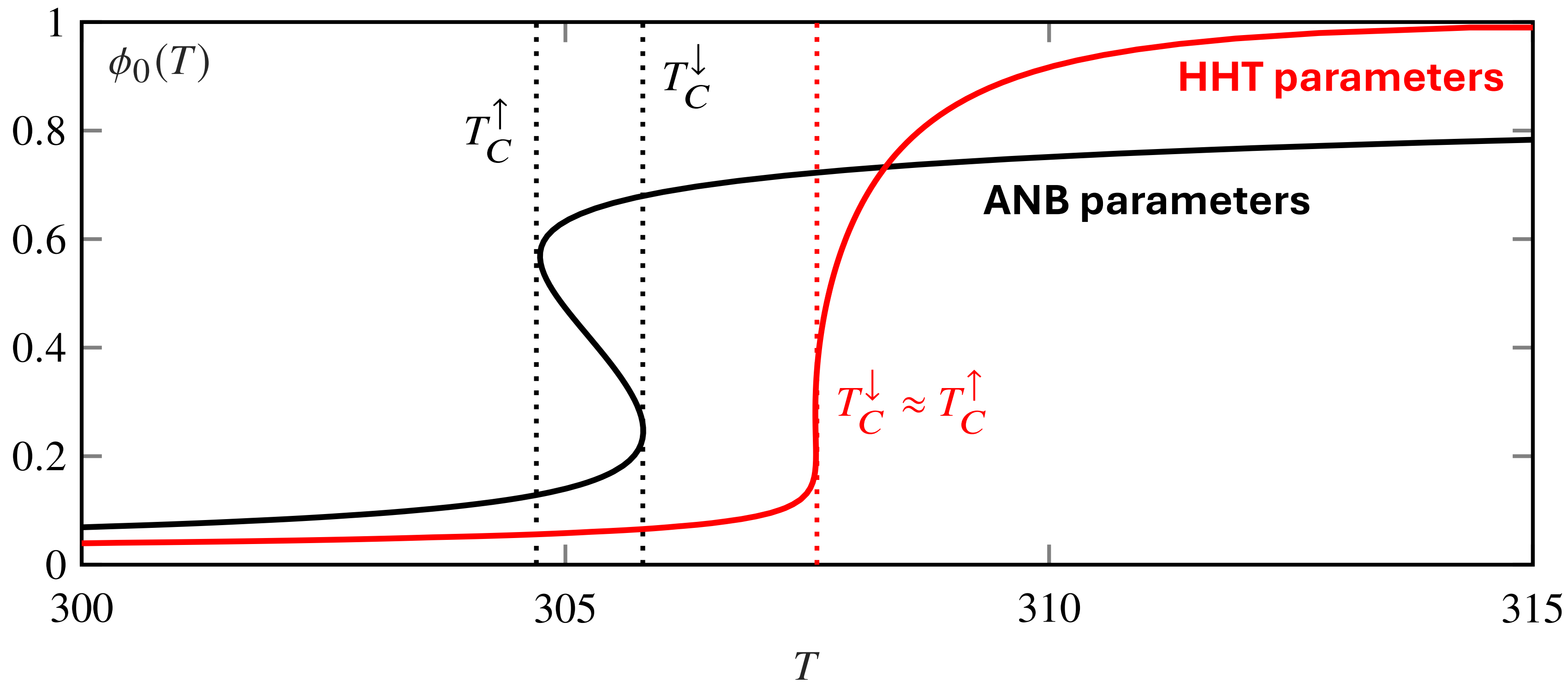
ANB parameters



HHT parameters



Osmotic pressures



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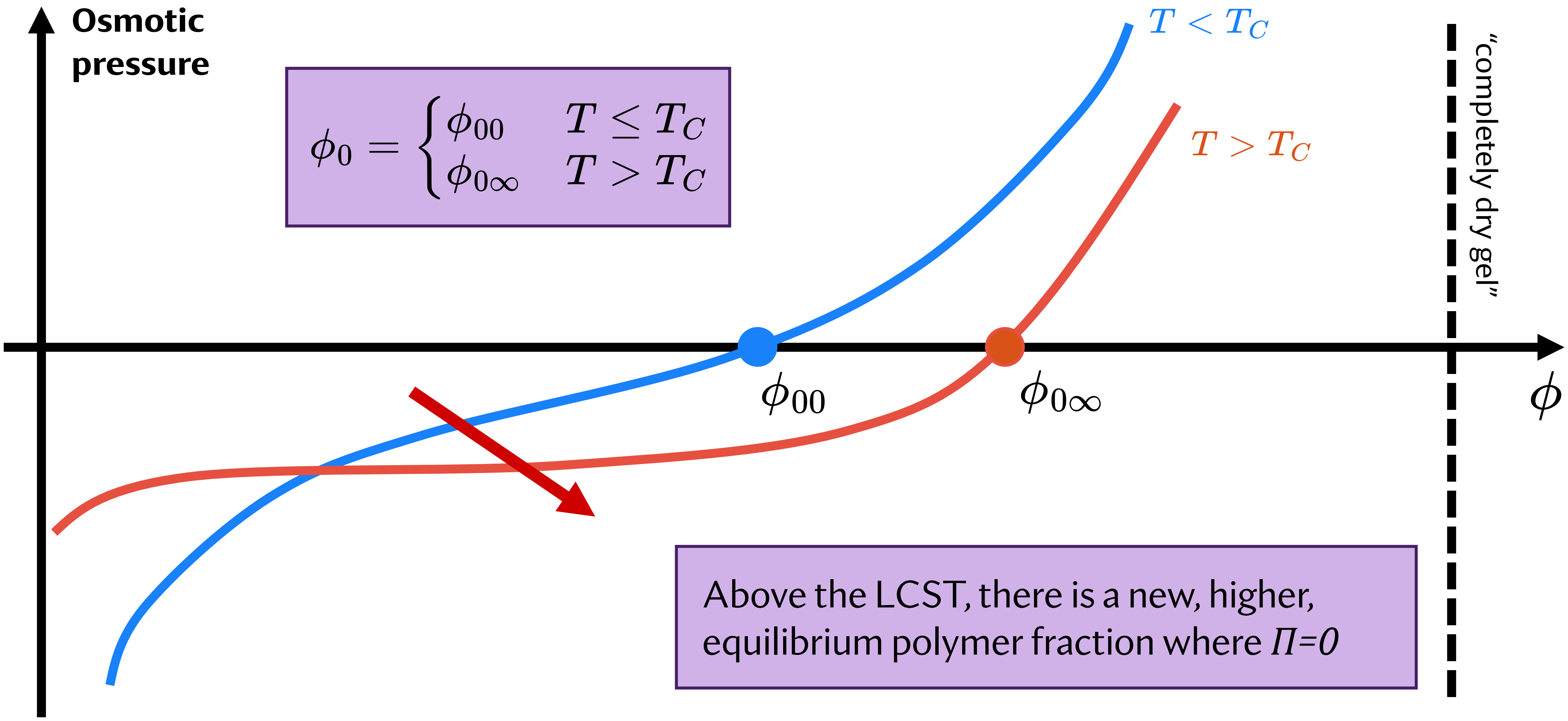
Phenomenological observations



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

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

The thermo-responsive LENS framework

Osmotic components

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

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

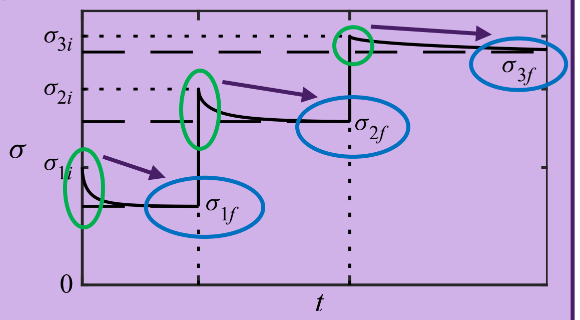
see Doi (2009)

LENS modelling

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

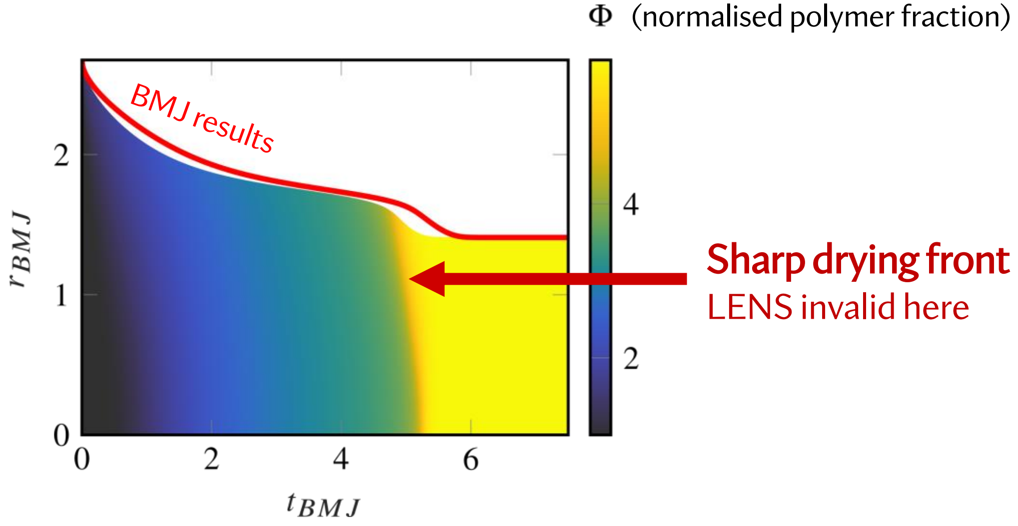
$$\frac{\partial \phi}{\partial t} + \boldsymbol{q}\cdot\boldsymbol{\nabla}\phi = \boldsymbol{\nabla}\cdot\left\{\frac{k(\phi)}{\mu_l}\left[\phi\frac{\partial \Pi}{\partial \phi} + \frac{4\mu_s(\phi)}{3}\left(\frac{\phi}{\phi_0}\right)^{1/3}\right]\boldsymbol{\nabla}\phi\right\}$$

Can feasibly measure osmotic pressure in a macroscopic experiment



Example: deswelling hydrogel bead in water

comparison with Butler & Montenegro-Johnson (2022)



Modelling temperature evolution

- Is this all? Is it reasonable to neglect heat contributions from swelling or drying? How about thermoelasticity?
- Furthermore, how is heat transferred through a responsive gel? Must couple influence from advection, diffusion, heat sources/sinks...

Heat transfer in porous media

Treats each phase separately, with a coupling term (e.g. $H(T_{water}-T_{polymer})$ or similar).

- Easy physical interpretation
- Matches nicely with continuum models

- Hard to couple heat sources/sinks and quantify coupling between phases

Thermoelasticity

Starts from the laws of thermodynamics and the free energy density function from before.

- Captures potentially complicated thermodynamics

- Hard to interpret some terms: **can LENS help?**

Modelling temperature evolution

μ **Chemical potential**
$=\Omega_f p$ (Peppin et al 2005)

Internal energy change
Take $U=cT$

External supply of heat
Ignore here

Heat generation (thermoelasticity)

$$\mathbf{F} \approx (\phi/\phi_{00})^{-1/3}\,\mathbf{I}$$

$$\frac{\mathrm{d}U}{\mathrm{d}t} = R - \boldsymbol{\nabla}\cdot\boldsymbol{Q} + \phi^{-1}\sigma\mathbf{F}^{-\mathsf{T}} : \frac{\mathrm{d}\mathbf{F}}{\mathrm{d}t} - \boldsymbol{J}\cdot\boldsymbol{\nabla}\mu + \mu\frac{\mathrm{d}C}{\mathrm{d}t}$$

Number density of water molecules

$$C = \frac{1}{\Omega_f}\left(\frac{1}{\phi} - 1\right)$$

Heat flux
Two components – transport of material *and* Fourier-type conduction

$$\boldsymbol{Q} = cT\boldsymbol{q} - c\kappa\boldsymbol{\nabla}T$$

Molecular flux of water

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

$$c\frac{\mathrm{d}T}{\mathrm{d}t} = c\,\boldsymbol{q}\cdot\boldsymbol{\nabla}T + \xcancel{cT\,\boldsymbol{\nabla}\cdot\boldsymbol{q}} - \frac{1}{3\phi^2}\frac{\partial\phi}{\partial t}\operatorname{tr}\sigma + \frac{k(\phi)}{\mu_l}|\boldsymbol{\nabla}p|^2 - \frac{p}{\phi^2}\frac{\partial\phi}{\partial t} + c\kappa\nabla^2T$$

$$\operatorname{tr}\sigma = -3P = -3(p+\Pi)$$

Modelling temperature evolution

“Latent heat of swelling or drying”
Energy used up or released in swelling/drying **and** heat generation by deformation. Dependent on [generalised] osmotic pressure.

Advection
Heat energy carried with deforming gel

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

Diffusion
(having assumed spatially-constant diffusivity)

Work done by pore flows
Viscous resistance as water flows through the gel pore spaces

N.B. this reduces down to simple diffusion when the gel isn’t reconfiguring

Modelling temperature evolution

$$\tau = \frac{\mu_l L^2}{k\hat{\Pi}}$$

$$\frac{\mathrm{D}_{\boldsymbol{q}}T}{\mathrm{D}t} = \frac{\partial T}{\partial t} + \boldsymbol{q}\cdot\boldsymbol{\nabla}T = \kappa\nabla^2 T + \frac{\Pi(\phi)}{c\phi^2}\frac{\partial\phi}{\partial t} + \frac{k(\phi)}{\mu_l c}|\boldsymbol{\nabla}p|^2$$

$$\frac{\Delta T}{\tau} \qquad \frac{\kappa\Delta T}{L^2} \qquad \frac{\hat{\Pi}}{c\tau}$$

- Can compare relative importance of heat transfer methods using two non-dimensional numbers,

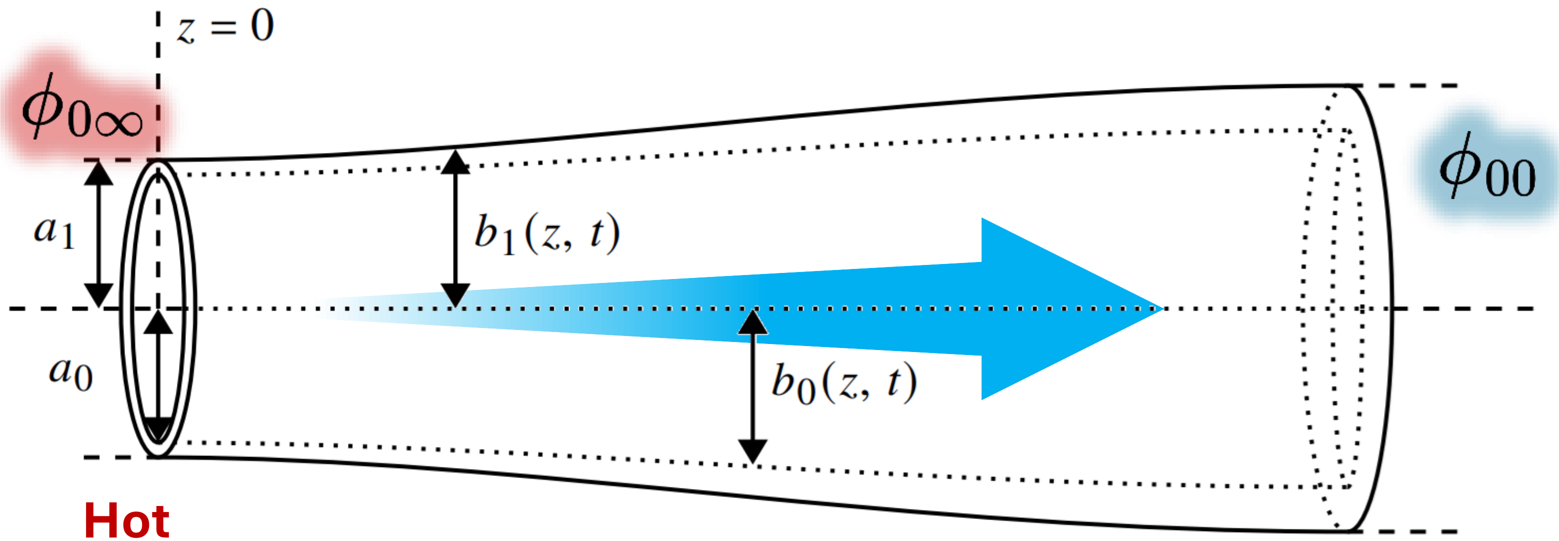
$$Le = \frac{\tau\kappa}{L^2} = \frac{\mu_l\kappa}{k\hat{\Pi}}$$

Typically ~*10*, so diffusion of heat dominates over compositional diffusion

$$\mathcal{D} = \frac{\hat{\Pi}}{c\Delta T}$$

Typically ~*1/ΔT*, so importance of swelling and interstitial flows depends on magnitude of temperature differential

Application: tubes of responsive gel



Hot

Shrunken tube, narrow lumen

$T = T_C + \Delta T$

Cold

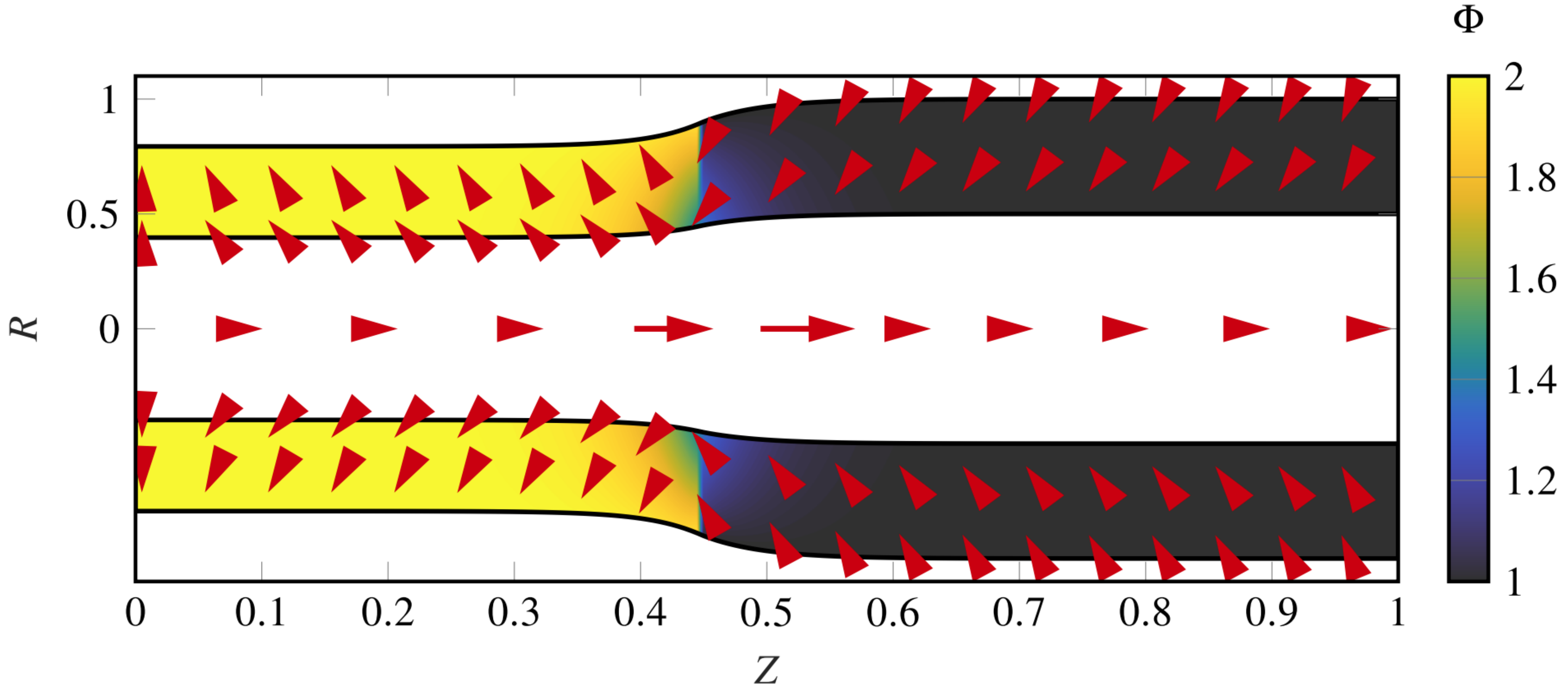
Relaxed tube, wide lumen

$T \to T_C$

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

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

Flows through the tube



Summary

- Modelling thermo-responsive gels requires an understanding of how the affinity of polymer chains for water changes with temperature

- This can be gained from microscopic models of the gel, or phenomenologically: spotting the LCST and how the equilibrium polymer fraction changes around it is enough to model the behaviour of these gels accurately

- We must be careful when there are sharp drying fronts, however – LENS can't handle these

- LENS does, however, allow us to carefully interpret all the terms in the heat transfer equation, closing the system

With thanks to

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