

# A 'linear' elastic theory for hydrogels

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# | Hydrogels

- Hydrophilic polymer scaffold takes on water and thus can expand by  $>500\%$  in volume from when dry.
- Applications include children's toys, absorbent nappies, contact lenses, wound dressings, water storage gels for pot plants.



# | Hydrogels

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## CheckNews

### Non, ce youtubeur alsacien n'a pas bouché les canalisations de son village avec des billes d'eau

Dans des vidéos virales dans le monde entier, Cyril Schreiner met en scène une prétendue «catastrophe» à base de canalisations de toilettes et de petites perles qui gonflent au contact de l'eau.



Capture d'écran Instagram (@cyrilacnir)

par [Vincent Copvas](#)  
publié le 3 mars 2020 à 15h06

Question posée par Julie le 28/02/2020

Bonjour,


## CheckNews

CheckNews, la newsletter. Recevez chaque midi les réponses à vos questions.

Je m'inscris

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Votre question fait référence à une série de vidéos virales du youtubeur Cyril Schreiner publiée notamment [sur Instagram](#). Dans celles-ci, le vidéaste explique avoir bouché l'ensemble de ses canalisations (et celles de ses voisins) à cause de «perles d'eau», des petites billes [qui gonflent une fois immergées dans de l'eau](#).



### Pourquoi l'armée israélienne a-t-elle annoncé une attaque terrestre à Gaza qui n'a pas eu lieu?

14 mai 2021

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poser une question mode d'emploi

#### LE PORTRAIT DU JOUR



**Barbie Stupel** a...

Libération, 28/02/2020



# | Hydrogels

- Hydrophilic polymer scaffold takes on water and thus can expand by  $>500\%$  in volume from when dry.
- Applications include children's toys, absorbent nappies, contact lenses, wound dressings, water storage gels for pot plants.
- Also occur naturally – cellulose, for example, is sufficiently hydrophilic to form hydrogels (with possible applications for bordered pits in plant xylem?)
- Usually studied as a 'bulk material' – solid and liquid phases are lumped together into one.



# | Why bother? The big picture

- It's clear that the properties of hydrogels arise from a number of different sources:
  - They exhibit elastic behaviour – not just a property of the polymer scaffold!
  - The polymer chains are hydrophilic – osmotic effects draw in water from the surrounds (it's this that leads to swelling).
  - Water can flow through the gel – as is the case in bordered pits of trees.
- All of this suggests treating them as a poroelastic medium, in the same way that one would soils or other deformable porous media.

# | Why bother? The big picture

- Currently there are two main ways to model the poroelastic behaviour of hydrogels:
  - **Nonlinear models (Gaussian-chain + Flory-Huggins) [Bertrand et al.]**  
Gel treated as a single phase, with the elastic and osmotic effects from the work-energy function; describes the gel chemically but analytically intractable and only suitable for numerical computation.
  - **Linear models [Doi, Biot, Tanaka-Hocker-Benedek etc.]**  
Describe stresses on the gel using linear-elastic theory. Mathematically very simple but only suitable for small strains (~10% maximum according to Landau & Lifshitz).
- So neither is ideal for swelling and drying!

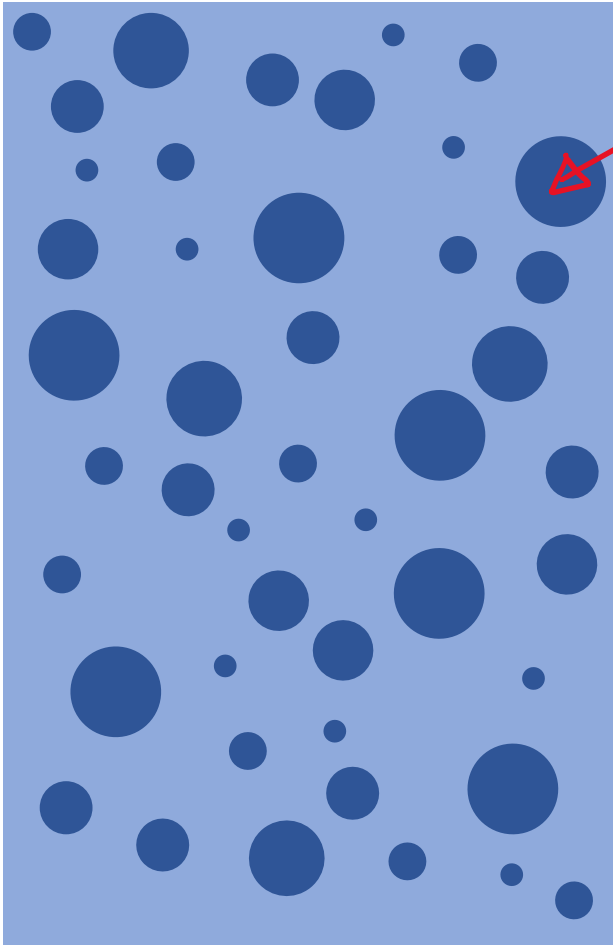
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**Bertrand, T. et al.** *Dynamics of swelling and drying in a spherical gel* Phys. Rev. Applied 6 (2016)

**Doi, M.** *Gel dynamics* J. Phys. Soc. Japan 78 (2009); **Biot, M. A.** *General theory of three-dimensional consolidation* J. Appl. Phys. 12 (1941); **Tanaka, T. et al.** *Spectrum of light scattered from a viscoelastic gel* J. Chem. Phys. 59 (1973)

**Landau, L. D. and Lifshitz, E. M.** *Theory of Elasticity* Butterworth-Heinemann (1986)

# | Pressure in hydrogels



## **Polymer fraction**

Denoted  $\phi$  - typically around  $10^{-2}$

## **Pervadic pressure $p$**

The pressure of the liquid phase of the colloid as measured by a manometer separated from the system by a partially-permeable membrane.

## **Bulk (thermodynamic) pressure $P$**

The force exerted per unit area by the whole system.

## **Osmotic pressure $\Pi$**

The difference between these two:  $P = p + \Pi$

# | Strains and deformation

- In gel swelling, expect *deviatoric* strains to be small but *isotropic* strains can be large. Lagrangian reference state  $\phi = \phi_0$  everywhere, take  $\mathbf{X} \rightarrow \mathbf{X} + \boldsymbol{\xi} = \mathbf{x}$ , then

$$\underline{\underline{\mathbf{F}}} = \nabla_{\mathbf{X}} \mathbf{x} \quad \text{with} \quad \det \underline{\underline{\mathbf{F}}} = \frac{\delta V}{\delta V_0} = \frac{\phi_0}{\phi}$$

- Let  $\underline{\underline{\mathbf{F}}} = \mathcal{F} \underline{\underline{\mathbb{I}}} + \underline{\underline{\mathbf{f}}}$  with the deviatoric part small. Then

$$\det \underline{\underline{\mathbf{F}}} = \mathcal{F}^n + \mathcal{O}(\underline{\underline{\mathbf{f}}}^2) \Rightarrow \mathcal{F} = \left( \frac{\phi_0}{\phi} \right)^{1/n}$$

- To recast in an Eulerian point of view, define the Cauchy strain tensor

$$\underline{\underline{\mathbf{e}}} = \frac{1}{2} (\nabla_{\mathbf{x}} \boldsymbol{\xi} + (\nabla_{\mathbf{x}} \boldsymbol{\xi})^T) = \underline{\underline{\mathbb{I}}} - \frac{1}{2} (\underline{\underline{\mathbf{F}}}^{-1} + \underline{\underline{\mathbf{F}}}^{-T})$$



# | Strains and deformation

- Taylor-expand to first order, with

$$\underline{\underline{\mathbf{F}}}^{-1} = \frac{1}{\mathcal{F}} \underline{\underline{\mathbb{I}}} - \frac{1}{2\mathcal{F}^2} \left( \underline{\underline{\mathbf{f}}} + \underline{\underline{\mathbf{f}}}^T \right) + \mathcal{O} \left( \underline{\underline{\mathbf{f}}}^2 \right)$$

$$\Rightarrow \underline{\underline{\mathbf{e}}} = \left[ 1 - \left( \frac{\phi}{\phi_0} \right)^{1/n} \right] \underline{\underline{\mathbb{I}}} + \underline{\underline{\boldsymbol{\epsilon}}}$$

**Compare with linear limit**

In linear elasticity,

$$\underline{\underline{\mathbf{e}}} = -\frac{\phi - \phi_0}{n\phi_0} \underline{\underline{\mathbb{I}}} + \underline{\underline{\boldsymbol{\epsilon}}}$$

**Deviatoric strain**

Assumed small (to check later). Equal to  $\frac{1}{2\mathcal{F}^2} \left( \underline{\underline{\mathbf{f}}} + \underline{\underline{\mathbf{f}}}^T \right)$

Which agrees with this in the  $\phi \rightarrow \phi_0$  limit.

# | Gel dynamics

- The polymer and water phases are individually incompressible and thus we can use a standard mass conservation approach to describe dynamics of gel constituents:

$$\frac{\partial \phi}{\partial t} + \nabla \cdot (\phi \mathbf{u}_p) = 0 \quad \text{and} \quad \frac{\partial (1-\phi)}{\partial t} + \nabla \cdot [(1-\phi) \mathbf{u}_l] = 0$$

- Let the Darcy (interstitial) velocity be  $(1-\phi)(\mathbf{u}_l - \mathbf{u}_p) = \mathbf{u}$ . Then  $\nabla \cdot \mathbf{u} + \nabla \cdot \mathbf{u}_p = 0$ .
- Combine with Darcy's law to find that

$$\nabla \cdot \mathbf{u}_p = \frac{\partial (\nabla \cdot \boldsymbol{\xi})}{\partial t} = \frac{\phi^{(1-n)/n}}{\phi_0^{1/n}} \frac{\partial \phi}{\partial t} = \frac{1}{\mu_l} \nabla \cdot [k(\phi) \nabla p]$$

- This relates polymer fractions to pervadic pressure gradients.

# | Towards a constitutive relation

- We now wish to relate gradients in  $p$  to gel properties  $\xi$  and  $\phi$ .
- Separate out the stress tensor into a part due to the solid and one due to the liquid:

$$\underline{\underline{\sigma}} = \phi \underline{\underline{\sigma}}_s + (1 - \phi) \underline{\underline{\sigma}}_l$$

- Assume a Newtonian constitutive relation for the fluid with viscosity  $\mu_l$  and follow Terzaghi in introducing an effective stress.

$$\underline{\underline{\sigma}} = \phi(\underline{\underline{\sigma}}_s + p \underline{\underline{\mathbb{I}}}) + 2(1 - \phi)\mu_l \underline{\underline{\varepsilon}} - p \underline{\underline{\mathbb{I}}}$$

- Neglect the viscous stresses and seek a form for the effective stress  $\underline{\underline{\sigma}}_e = \phi(\underline{\underline{\sigma}}_s + p \underline{\underline{\mathbb{I}}})$ .

# | Linear-elastic-nonlinear-swelling approach

- Linear elasticity assumes  $\underline{\underline{\sigma}}_e = \underline{\underline{\mathbf{C}}} : \underline{\underline{\mathbf{e}}}$  for some constant tensor  $\underline{\underline{\mathbf{C}}}$ , then by isotropy

$$\underline{\underline{\sigma}}_e = \left( K \operatorname{tr} \underline{\underline{\mathbf{e}}} \right) \underline{\underline{\mathbb{I}}} + 2\mu_s \underline{\underline{\mathbf{e}}}$$

- We allow  $\underline{\underline{\mathbf{C}}}$ , and thus the material properties, to depend on  $\phi$ , and thus, by a similar argument, have

$$\underline{\underline{\sigma}}_e = f(\phi) \underline{\underline{\mathbb{I}}} + 2\mu_s(\phi) \underline{\underline{\mathbf{e}}} = -K(\phi) \frac{\phi - \phi_0}{\phi_0} \underline{\underline{\mathbb{I}}} + 2\mu_s(\phi) \underline{\underline{\mathbf{e}}}$$

$$\underline{\underline{\sigma}} = - \left[ p + K(\phi) \frac{\phi - \phi_0}{\phi_0} \right] \underline{\underline{\mathbb{I}}} + 2\mu_s(\phi) \underline{\underline{\mathbf{e}}}$$

Shear modulus

Osmotic modulus

# | Linear-elastic-nonlinear-swelling approach

- Material properties are described by just four parameters ( $K$ ,  $\mu_s$ ,  $\phi_0$  and  $k$ ) with governing equation and constitutive relation

$$\frac{\partial \phi}{\partial t} = \frac{\phi_0^{1/n} \phi^{(n-1)/n}}{\mu_l} \nabla \cdot [k(\phi) \nabla p] \quad \text{and} \quad \underline{\underline{\sigma}} = - \left[ p + K(\phi) \frac{\phi - \phi_0}{\phi_0} \right] \underline{\underline{\mathbb{I}}} + 2\mu_s(\phi) \underline{\underline{\epsilon}}.$$

- Still need to justify neglecting viscous terms. Scaling argument:

$$\frac{\text{viscous}}{\text{elastic}} \sim \frac{(1 - \phi_0)\mu_l u_l}{\mu_s u_p t_{el}} \sim \frac{\phi_0 \mu_l}{\mu_s t_{el}} \sim \frac{\phi_0 k_0 K}{\mu_s L^2} \ll 1$$

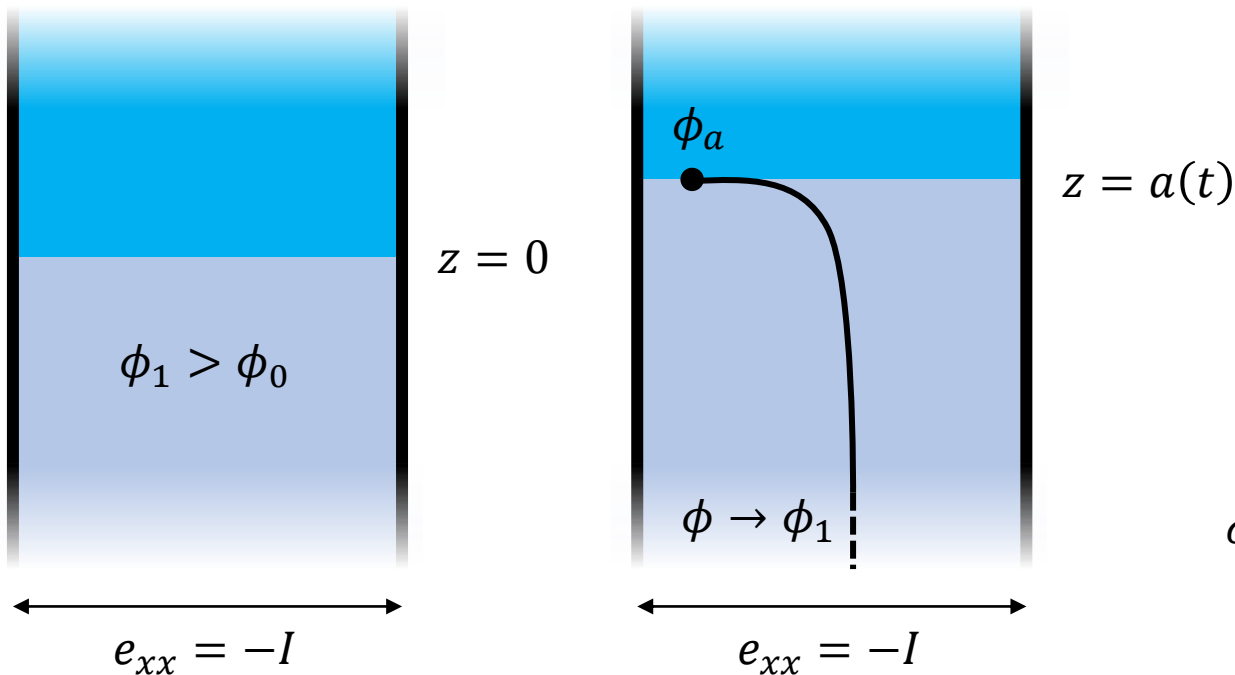
$t_{el} \sim \mu_l L^2 / k_0 K$ , letting  $p \sim K$

$K/\mu_s \sim 1$  and  $k_0 \sim 10^{-15} \text{ m}^2$



# | A first, one-dimensional, problem

- Take partially-dried hydrogel confined horizontally, with uniform polymer fraction  $\phi_1 > \phi_0$ . The confinement means that the gel can't swell any more in the horizontal direction, but will swell vertically.
- The confinement also means we can express  $\epsilon_{zz}$  in terms of  $I$  and  $\phi$ .



$$1 - \left( \frac{\phi}{\phi_0} \right)^{\frac{1}{2}} + \epsilon_{xx} = e_{xx}$$

$$\Rightarrow \epsilon_{zz} = -\epsilon_{xx} = (1 + I) - \left( \frac{\phi}{\phi_0} \right)^{\frac{1}{2}}$$

$$\sigma_{zz} = - \left( p + K(\phi) \frac{\phi - \phi_0}{\phi_0} \right) + 2\mu_s(\phi) \left[ (1 + I) - \left( \frac{\phi}{\phi_0} \right)^{\frac{1}{2}} \right]$$

# | A first, one-dimensional, problem

$$\sigma_{zz} = -\left(p + K \frac{\phi - \phi_0}{\phi_0}\right) + 2\mu_s \left[ (1 + I) - \left(\frac{\phi}{\phi_0}\right)^{\frac{1}{2}} \right]$$

- The equation of equilibrium  $\partial\sigma_{zz}/\partial z = 0$  gives an expression for  $\partial p/\partial z$ . Substitute into polymer conservation law to get

$$\frac{\partial\phi}{\partial t} = \frac{\phi_0^{1/2}\phi^{1/2}}{\mu_l} \frac{\partial}{\partial z} \left[ k(\phi) \left\{ \frac{K(\phi)}{\phi_0} + \frac{\phi - \phi_0}{\phi_0} \frac{\partial K}{\partial\phi} + \frac{\mu_s(\phi)}{\phi_0^{1/2}\phi^{1/2}} - 2 \left[ (1 + I) - \left(\frac{\phi}{\phi_0}\right)^{1/2} \right] \frac{\partial\mu_s}{\partial\phi} \right\} \frac{\partial\phi}{\partial z} \right] (!)$$

**“Diffusivity”** increases for larger  $K$ ,  $k$ , smaller  $\mu_l$

- Boundary condition at interface:  $p = \sigma_{zz} = 0$  at  $z = a(t)$  - this sets interfacial  $\phi$ .
- Conservation of polymer sets  $\int_{-\infty}^{a(t)} (\phi - \phi_1) dz + \phi_1 a(t) = 0$ .
- This is messy – but powerful. Take  $K$ ,  $\mu_s$ ,  $k_0$  to be constant, and it looks altogether more familiar in the limit  $\phi \rightarrow \phi_0$ .

# | A first, one-dimensional, problem

- In the “fully linear” (Biot) limit, we’re left with a problem that can easily be solved analytically.

$$\frac{\partial \phi}{\partial t} = \frac{k_0(K + \mu_s)}{\mu_l} \frac{\partial^2 \phi}{\partial z^2}$$

$$\phi \rightarrow \phi_0(1 + 2I) \text{ as } z \rightarrow -\infty$$

$$\phi = \phi_0[1 + 2\mu_s I / (K + \mu_s)] \text{ at } z = a(t)$$

$$\dot{a} = - \frac{k_0(K + \mu_s)}{\mu_l} \frac{\partial \phi}{\partial z} \bigg|_{z=a(t)}$$

## Interfacial boundary condition

Interfacial polymer fraction comes from setting  $\Pi(\phi) = 2\mu_s \epsilon_{zz}$

## Far-field boundary condition

Assume isotropic swelling so  $\underline{\underline{e}} = -I \underline{\underline{I}}$  and thus  $\phi_1 = \phi_0(1 + 2I)$

# | A first, one-dimensional, problem

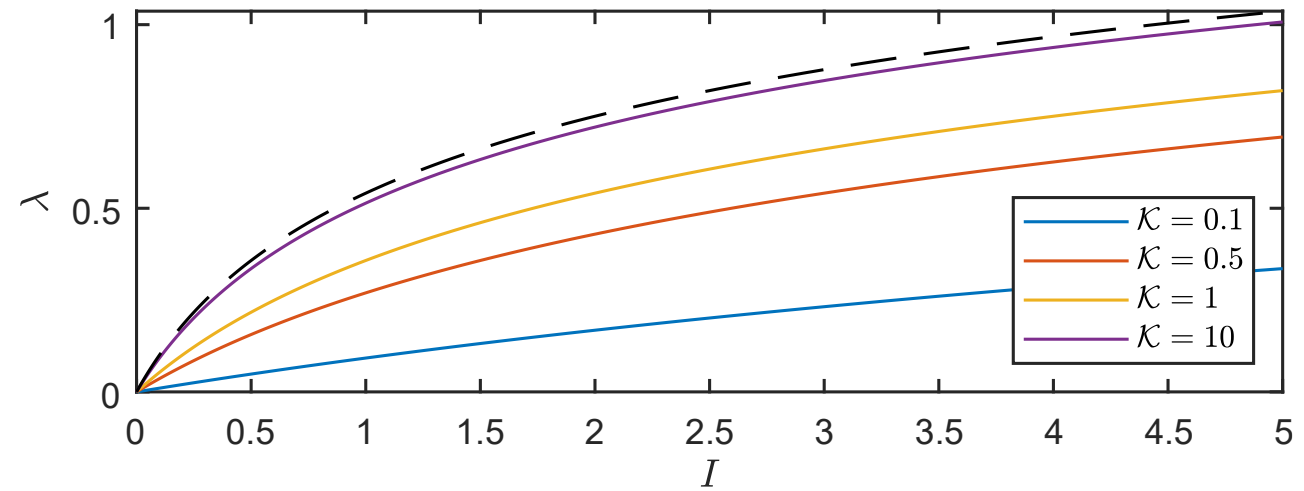
$$\phi = \phi_0 \left[ 1 + 2I \left( 1 - \frac{\mathcal{K}}{1 + \mathcal{K}} \frac{\text{erfc}(-\eta)}{\text{erfc}(-\lambda)} \right) \right]$$

$$a(t) = 2\lambda\sqrt{Dt}$$

with

$$\mathcal{K} = K/\mu_s, D = \frac{k_0(\mu_s + K)}{\mu_l} \text{ and}$$

$$\sqrt{\pi}\lambda e^{\lambda^2} \text{erfc}(-\lambda) = \frac{2I\mathcal{K}}{1 + \mathcal{K}} = \frac{\phi_1 - \phi_a}{\phi_0}$$



- Growth rate is dependent on the contrast between initial and final polymer fraction; more 'confinement' implies faster growth.
- Remark: the growing interface is linearly unstable here – instability can be analysed with Biot's approach.

# | Swelling of a hydrogel bead

- Problem has been considered by many authors both in nonlinear [Bertrand et al.] and linear [Punter *et al.*] contexts.
- We want a *post-hoc* justification that the assumption of large isotropic strains but small deviatoric strains is valid.

## Problem setup

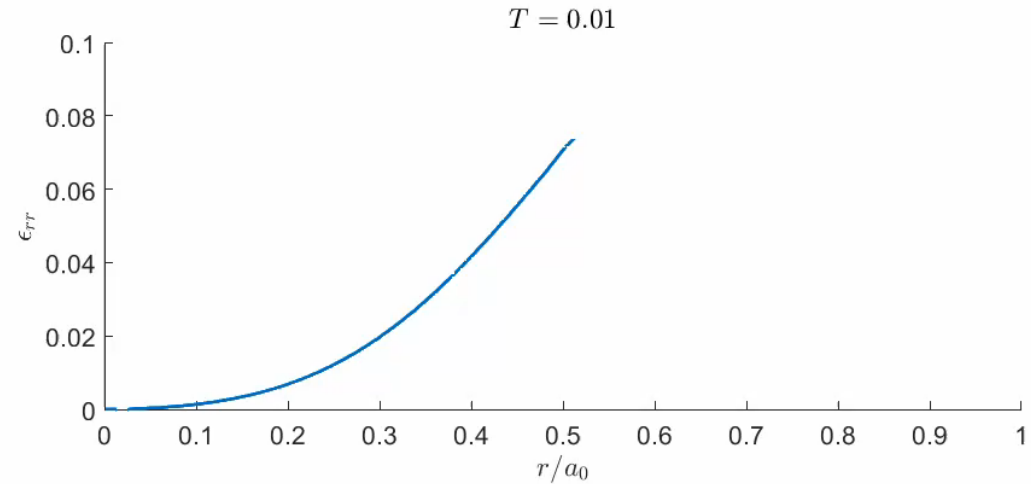
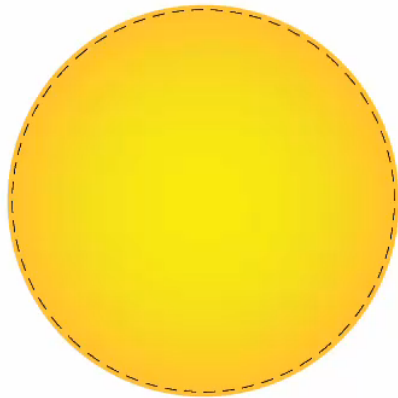
- Spherical bead with uniform polymer fraction  $\phi_1 > \phi_0$  placed in bulk water.
- Force-free, so  $\nabla \cdot \underline{\underline{\sigma}} = \mathbf{0}$  sets a relation between  $p$  and the other variables.
- Pervadic pressure and radial stress continuous across interface so  $p = 0$  and  $\sigma_{rr} = 0$  here as a boundary condition.
- Assume  $k(\phi) = k_0$  and  $\mu_s, K$  constants (for now).



# | Swelling of a hydrogel bead

$$\frac{K}{\mu_s} = 0.025 \text{ and } \phi = 8\phi_0 \text{ initially}$$

$$\epsilon_{rr} = \frac{2}{3} \left( \frac{\partial \xi}{\partial r} - \frac{\xi}{r} \right) = 2 \left[ 1 - \frac{\xi}{r} - \left( \frac{\phi}{\phi_0} \right)^{1/3} \right] \ll 1?$$



Boundary condition becomes

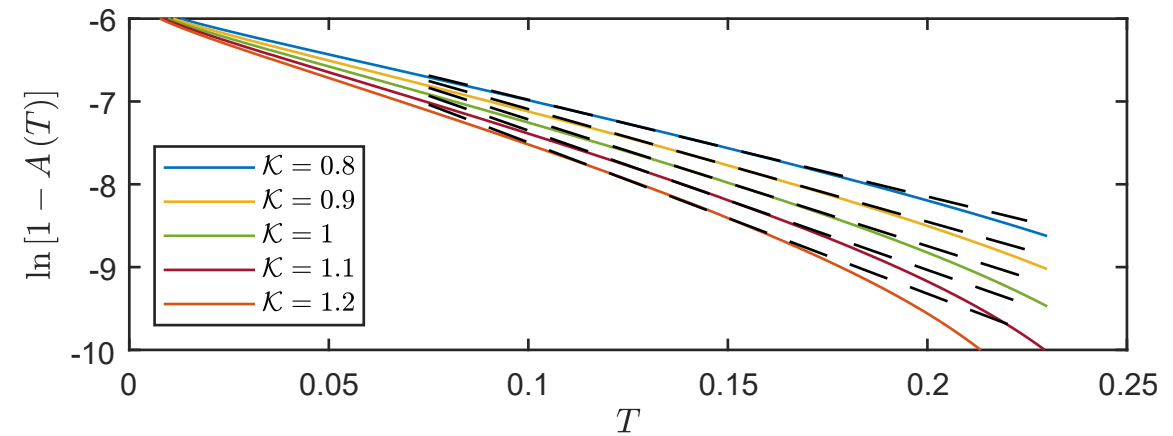
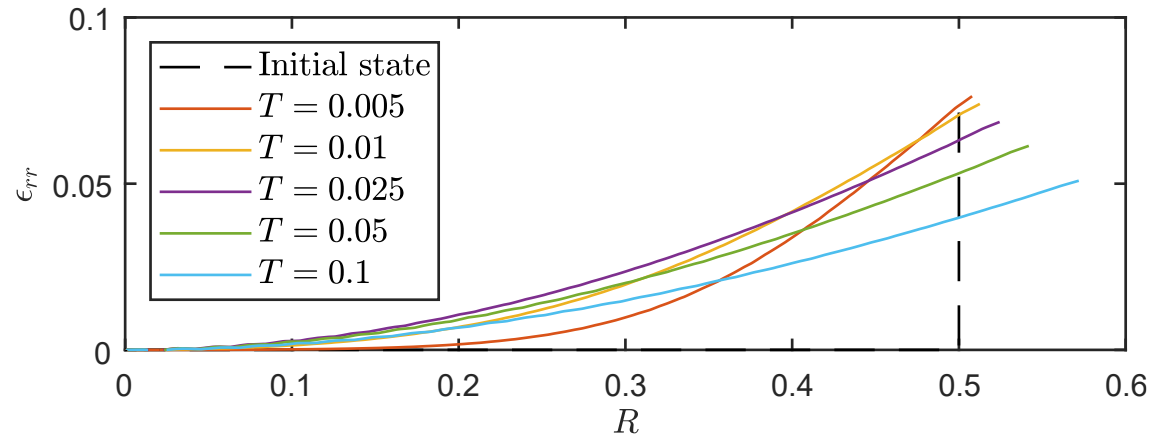
$$K \frac{\phi - \phi_0}{\phi_0} = 2\mu_s \epsilon_{rr}$$

on  $r = a(t)$ .



# Swelling of a hydrogel bead

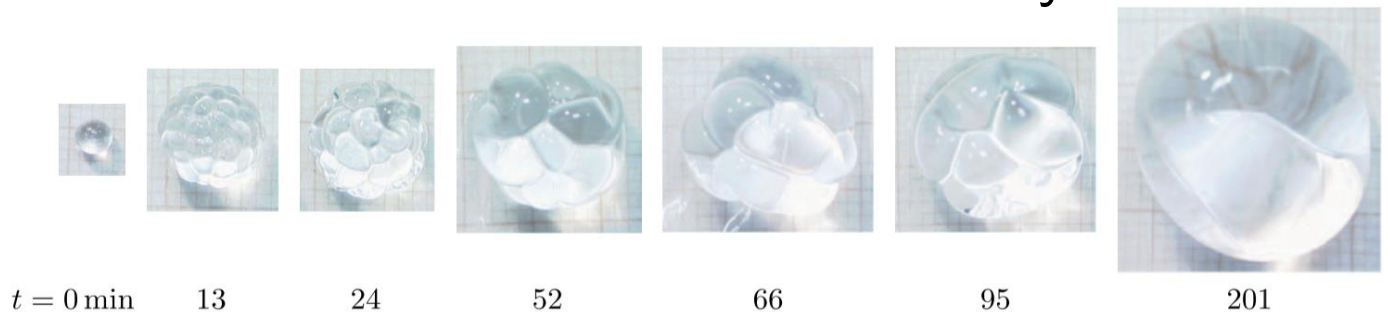
- Thus, can model swelling at very large strains but the transient state never has large deviatoric strains – which supports the initial assumptions of our model.



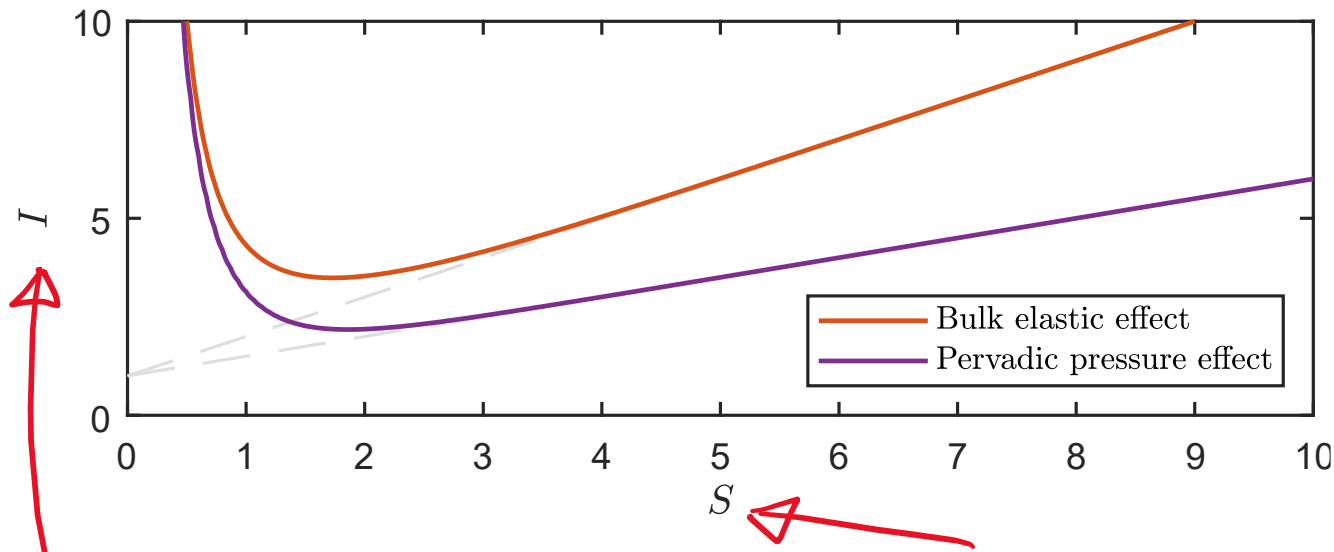
- This model also agrees well with existing linear models in the limit of small swelling, such as that of Punter *et al.* (as shown above).

# | Where next?

- Aim to investigate surface tension effects at curved interfaces – such effects are well-documented in the literature.
- How does the surface tension arise; is it a discontinuity in elastic stress or a discontinuity in the pervadic pressure which creates the condition  $\left[ \underline{\underline{\sigma}} \cdot \underline{\underline{n}} \right]_{-}^{+} = \gamma \kappa \underline{\underline{n}}$  (ideally we want the latter, but how to check this?)
- First idea – consider the aforementioned swelling instability for hydrogels – do we get qualitatively different behaviour if surface tension is introduced differently?



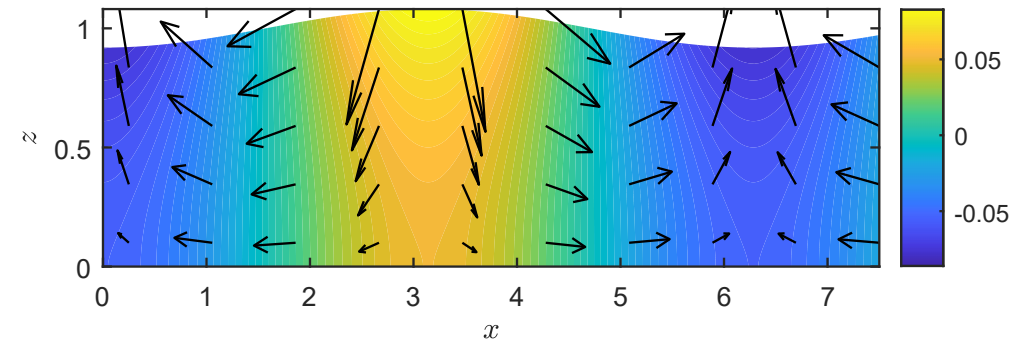
# | Where next?



**Compression for marginal stability**

The value of  $I$  at which the system is marginally stable

**Normalised wavenumber**



Making the discontinuity one in pervadic pressure drives a destabilising interstitial flow through the hydrogel matrix which quantitatively, but not qualitatively, destabilises the situation.

# | Conclusions

- Have developed a theory which couples linear elasticity in deviatoric strains with nonlinear behaviour in isotropic (swelling) strains both in constitutive relations and dynamical equations.
- This has the advantages of being analytically tractable but also captures perhaps the most important behaviour of hydrogels – the fact they can swell greatly.
- Next steps involve considering surface tension effects – can we quantify what the mechanism is behind this?
- Also seek constitutive relations for gels, using rheometry.