Buckling and swelling instabilities of super-absorbent gels

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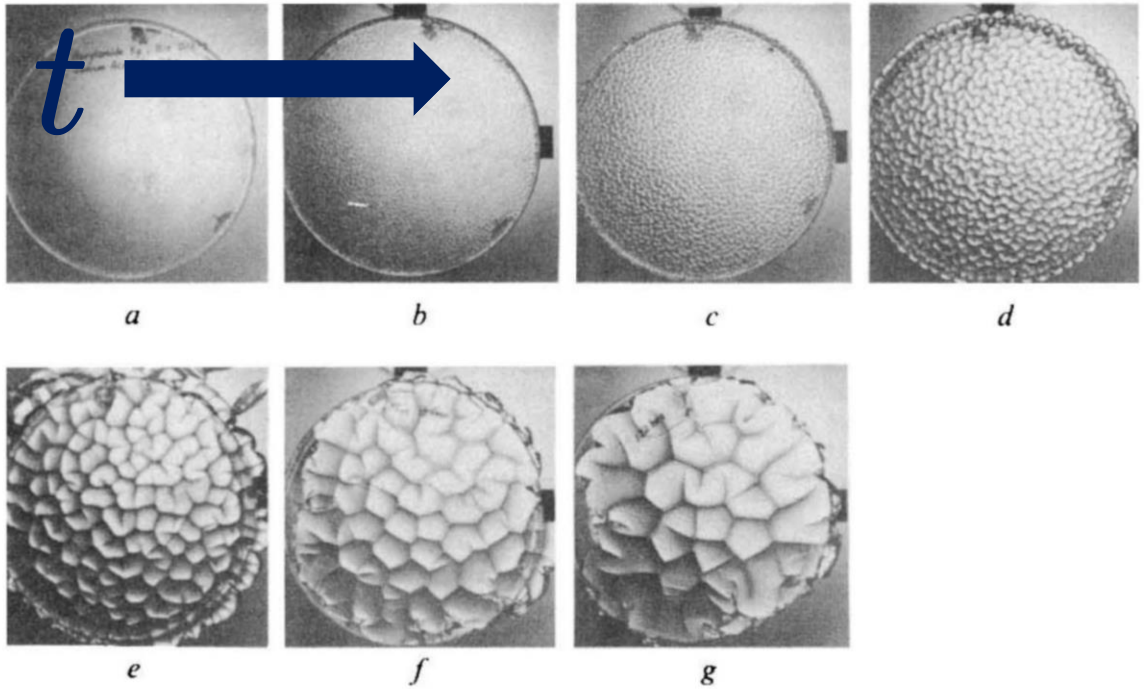
Swelling of confined gels

- When water is introduced to a 'dry' gel subject to mechanical confinement, wrinkles can form
- Swelling produces horizontal compressive stresses relieved by buckles



- Some gels form wrinkles, some don't; what's the criterion?
- Patterns smooth in time (wavelength grows like $t^{1/2}$)
- In some cases, patterns disappear
- **How do wrinkles grow?**

Buckling and swelling instabilities of super-absorbent gels

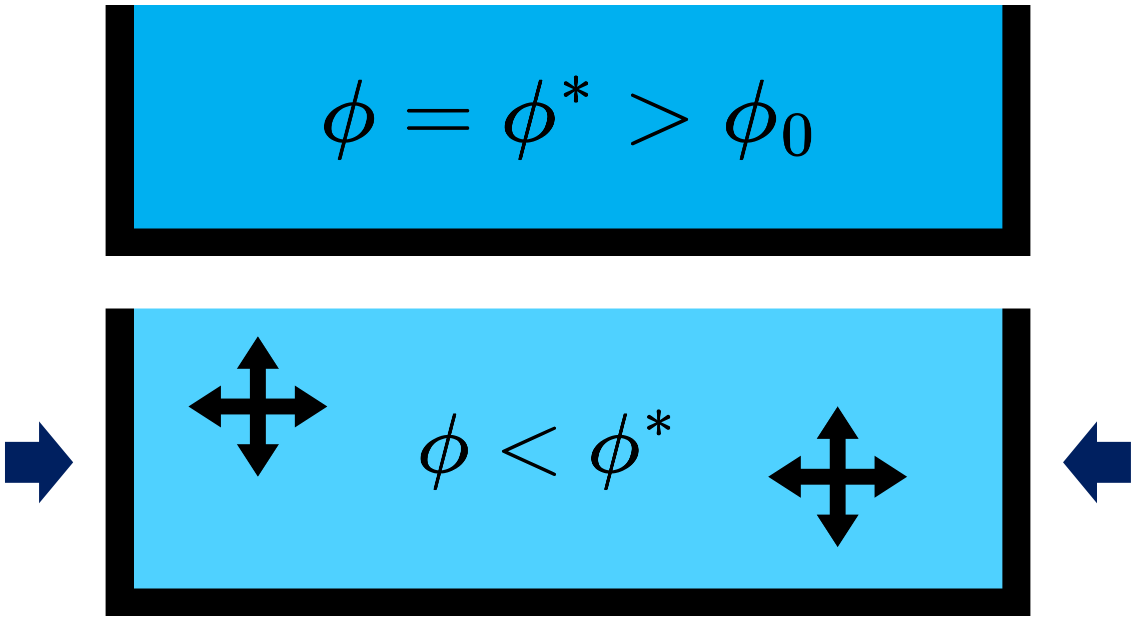
Figure from Tanaka *et al.*, Nature **325**:796-798, 1987

Physical setup

ϕ polymer volume fraction

ϕ_0 equilibrium (free swelling) polymer volume fraction

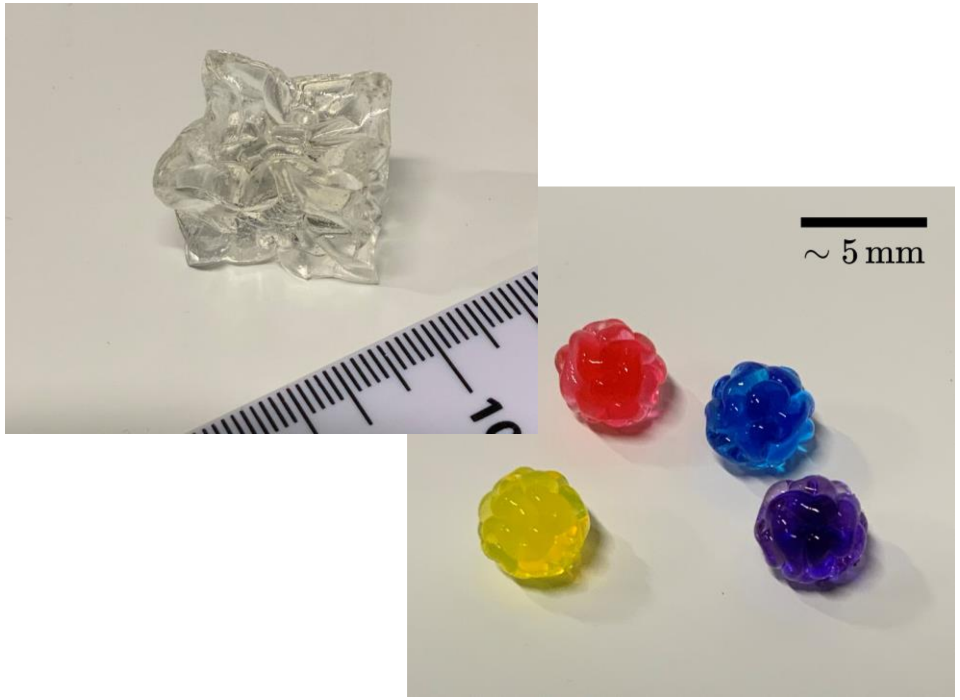
✓ Mechanically-confined swelling



$$\phi = \phi^* > \phi_0$$

$$\phi < \phi^*$$

✗ Confinement from differential swelling



Poromechanical modelling

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

Displacement-strain relations

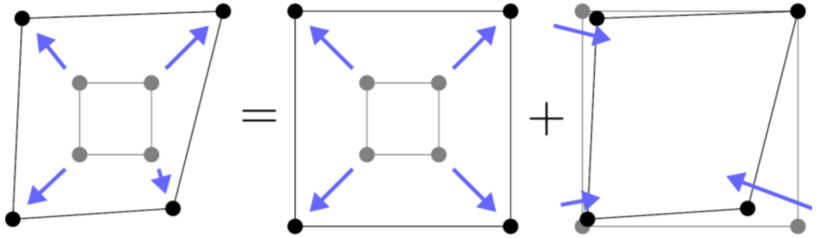
$$\mathbf{e} = \frac{1}{2}\left[\boldsymbol{\nabla}\boldsymbol{\xi} + \boldsymbol{\nabla}\boldsymbol{\xi}^{\mathrm{T}}\right]$$

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

Deviatoric strain tensor

$$\boldsymbol{\nabla}\cdot\boldsymbol{\xi} = 2\left[1 - \left(\frac{\phi}{\phi_0}\right)^{1/2}\right]$$

- Start with the gel in a reference configuration where polymer fraction equals ϕ_0 everywhere
- Take displacements $\boldsymbol{\xi}$ relative to this state and derive the Cauchy strain tensor as usual
- **Key idea:** isotropic strains can be small, but linearise around deviatoric strains
- A gel, swollen to a given degree, is a linear elastic material with its own properties



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$$\boldsymbol{\nabla}\cdot\boldsymbol{\xi} = 2\left[1 - \left(\frac{\phi}{\phi_0}\right)^{1/2}\right]$$

Constitutive relation

Shear modulus

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

Effective stress

Osmotic pressure

Pervadic (pore) pressure

- Remain agnostic as to the specific elastic model
- Pressure comes from isotropic elasticity and hydrophilic interactions

Example: Hencky elasticity

$$\boldsymbol{\sigma}^{(e)} = \Lambda(\phi/\phi_0)\,\mathrm{tr}(\mathbf{H})\mathbf{I} + (M-\Lambda)(\phi/\phi_0)\mathbf{H} \qquad \mathbf{H} = \frac{1}{2}\ln\left(\mathbf{F}\mathbf{F}^{\mathrm{T}}\right)$$

$$\Pi(\phi) = \left(\Lambda + \frac{M}{2}\right)\frac{\phi}{\phi_0}\ln\left(\frac{\phi}{\phi_0}\right) \qquad \mu_s(\phi) = \frac{M-\Lambda}{2}\left(\frac{\phi}{\phi_0}\right)^{2/3}$$

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Constitutive relation

Shear modulus
Assume constant

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

Pervadic (pore) pressure

Osmotic pressure
Assume linear, $\Pi = K(\phi - \phi_0)/\phi_0$

Transport equation

$$\frac{D_{\boldsymbol{q}}\phi}{Dt} = \boldsymbol{\nabla}\cdot\left\{\frac{k(\phi)}{\mu_l}\left[\frac{K\phi}{\phi_0} + \mu_s(\phi)\left(\frac{\phi}{\phi_0}\right)^{1/2}\right]\boldsymbol{\nabla}\phi\right\}$$

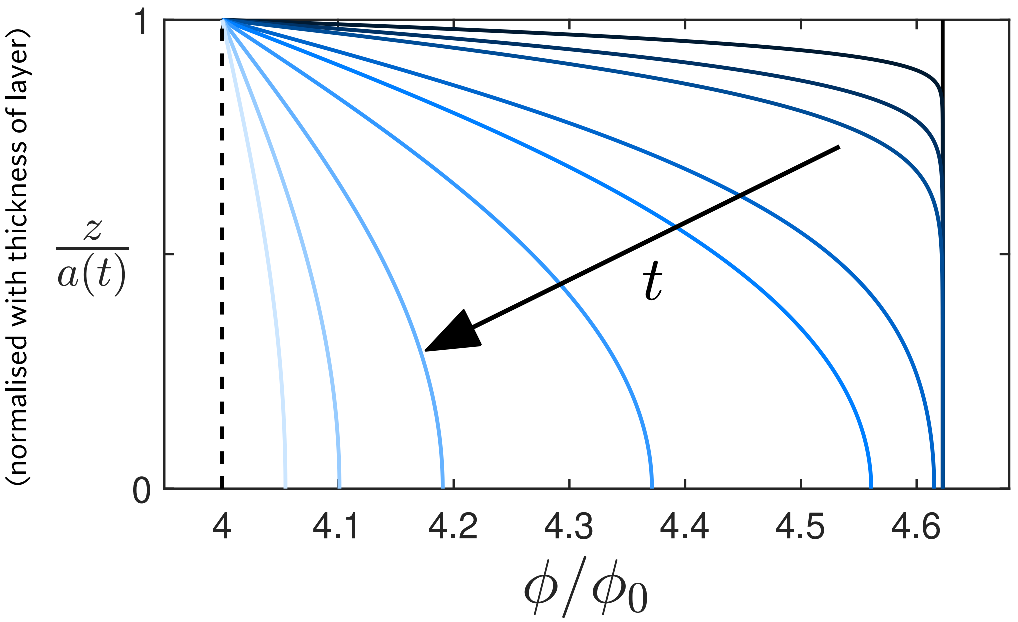
Advect with total flux

Coefficient from Darcy's law
Permeability over viscosity; assume constant

- Continuity of normal and tangential stress
- Fixed base
- Continuity of pore pressure

Boundary conditions

Confined swelling base state

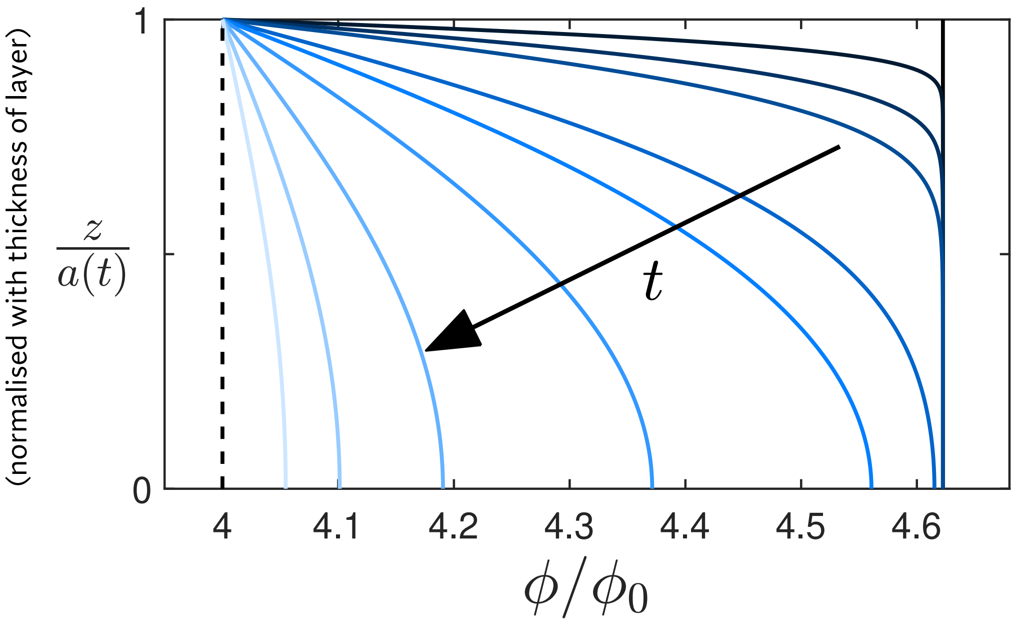


- The interface immediately swells to its equilibrium polymer fraction
- Water diffuses into the bulk to swell the rest of the layer
- Final steady state reached with uniform polymer fraction $\Phi_1 = \phi_1/\phi_0$

$$\sigma_{zz} = -K(\Phi - 1) + 2\mu_s \epsilon_{zz} = -K(\Phi - 1) - 2\mu_s \epsilon_{xx}$$
$$e_{xx} = 1 - {\Phi^*}^{1/2} = 1 - \Phi^{1/2} + \epsilon_{xx}$$

$$\Rightarrow \quad K(\Phi_1 - 1) = 2\mu_s \left({\Phi^*}^{1/2} - \Phi_1^{1/2} \right)$$

Confined swelling base state



- At very early times, diffusion only penetrates a small depth into the gel layer, and so we can approximate it as infinite depth

- Here, there exists a similarity solution for polymer fraction

$$\phi = \phi^* \left[1 - \left(1 - \frac{\phi_1}{\phi^*} \right) \frac{\operatorname{erfc}(-\chi)}{\operatorname{erfc}(-\lambda)} \right]$$

$$a(\tau) = a^* \left[1 + 2\lambda \sqrt{\left(\Phi^* + \mathcal{M} {\Phi^*}^{1/2} \right) \tau} \right] \qquad (\tau \ll 1)$$

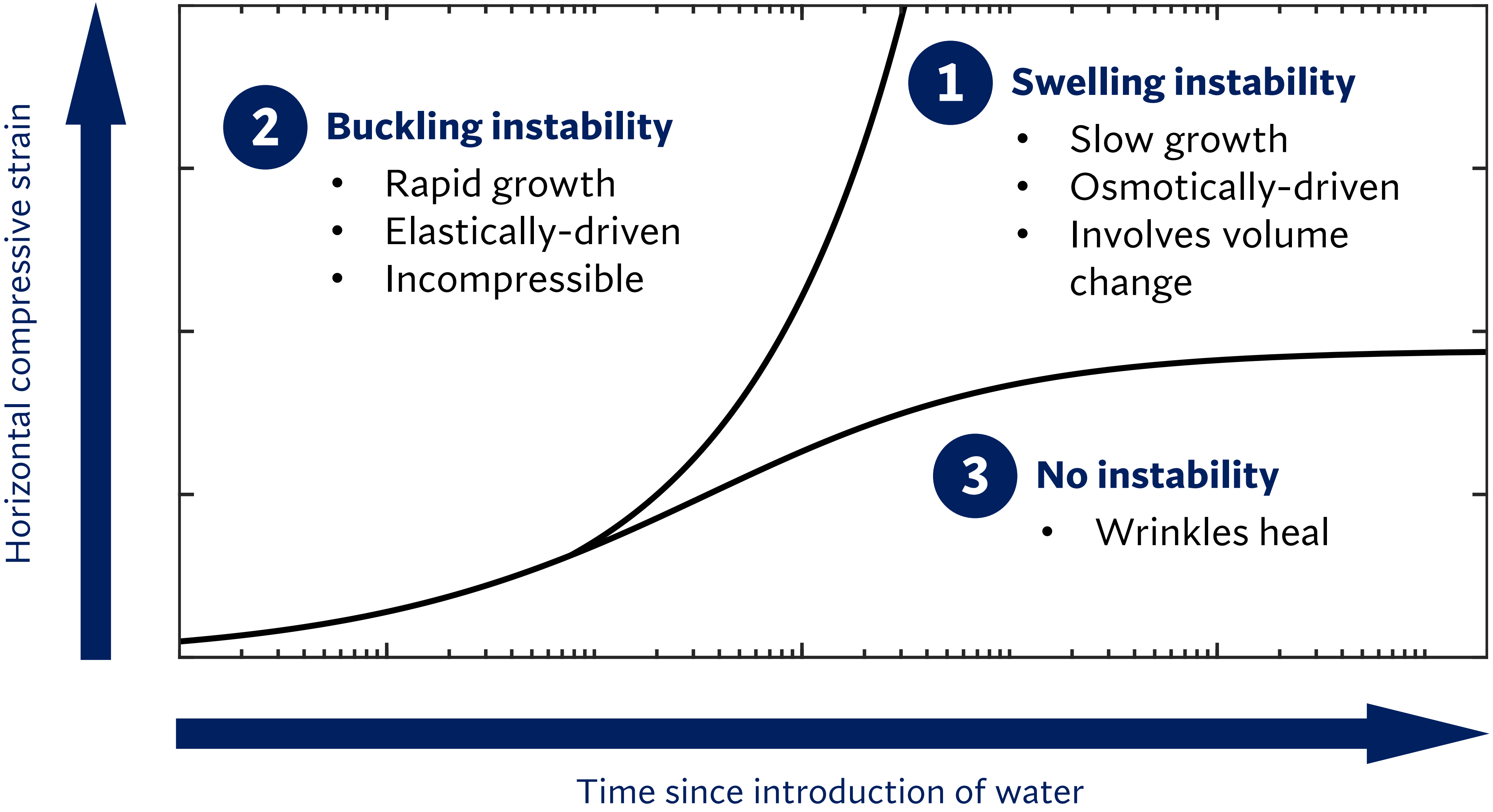
Initial thickness

Time, scaled with poroelastic timescale

$$\chi = \frac{z - a^*}{2a^* \sqrt{\left(\Phi^* + \mathcal{M} {\Phi^*}^{1/2} \right) \tau}}$$

$$\sqrt{\pi} \lambda e^{\lambda^2} \operatorname{erfc}(-\lambda) = \frac{\phi^*}{\phi_1} - 1$$

$= \mu_s / K$



② Buckling instability
- Rapid growth
- Elastically-driven
- Incompressible

① Swelling instability
- Slow growth
- Osmotically-driven
- Involves volume change

③ No instability
- Wrinkles heal

Buckling and swelling instabilities of super-absorbent gels

Swelling instability

- First, consider the case where $\Phi \equiv \Phi_1$ and there are no polymer fraction gradients (i.e. the final steady state); seek linear unstable modes

- Perturb the displacement field with sinusoidal modes and get growth rates from the swelling equation

- Cauchy's momentum equation
- Swelling equation

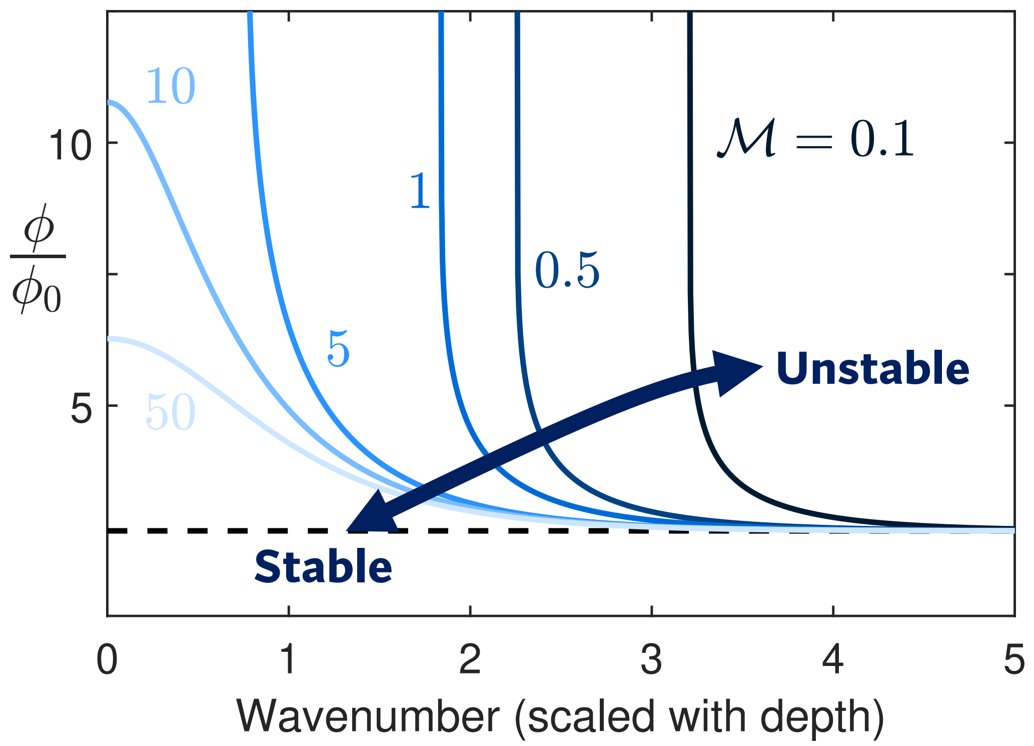
- No shear on base
- No normal displacement on base
- No shear on free surface
- No normal stress on free surface
- Continuity of pore pressure

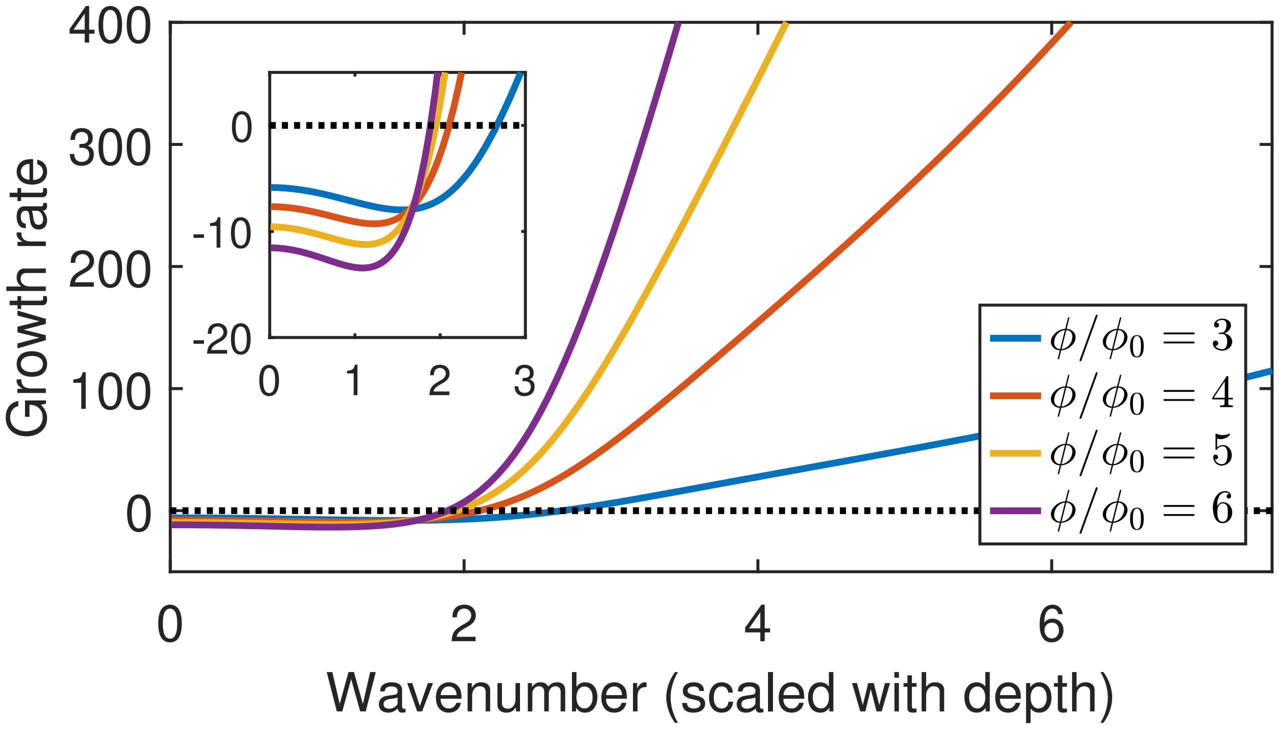
$= \mu_s/K$

$$\frac{\mathcal{M}s}{2\alpha}\sinh(2\alpha) + (\mathcal{M}+\Phi_1-1)\left(s+\mathcal{M}\Phi_1^{\frac{1}{2}}\alpha\sinh(2\alpha)\right) = 2\mathcal{M}\Phi_1^{\frac{1}{2}}(\mathcal{M}+\Phi_1-1)\sqrt{\alpha^2+\frac{s}{D}}\times \cosh^2(\alpha)\tanh\left(\sqrt{\alpha^2+\frac{s}{D}}\right)$$

+ no unstable incompressible modes – instability only grows *via* swelling!

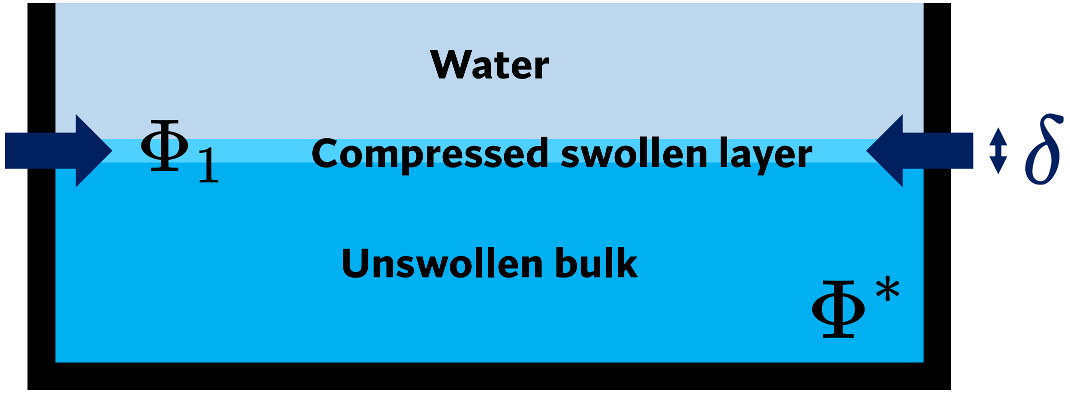
Swelling instability



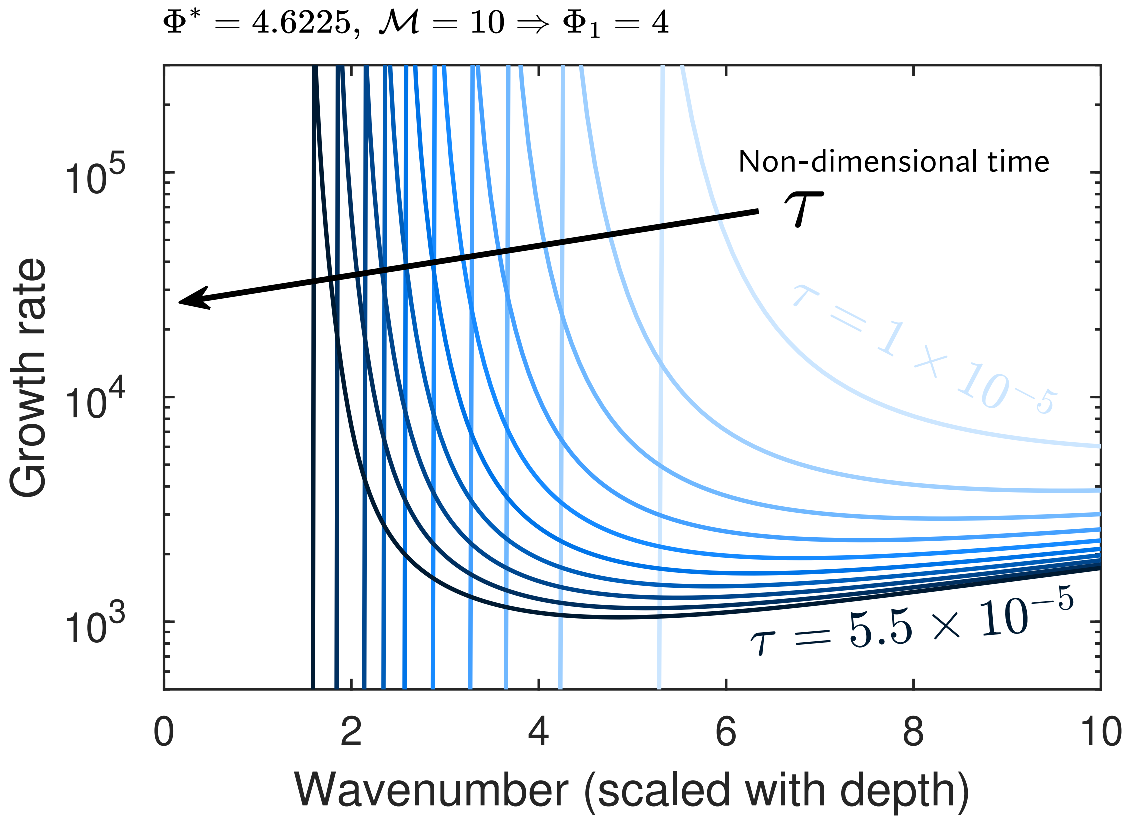


- Anchoring from the base stabilises long wavelength ripples
- Growth is faster with more compressive strain
- Criterion for instability is weaker with a greater shear modulus $\mathcal{M} = \mu_s/K$

The transient state



- There’s an apparent peak in growth rates at a finite wavenumber
- Fast growth – different mechanism
- Approach late-time limit
- Is this an elastic buckle?



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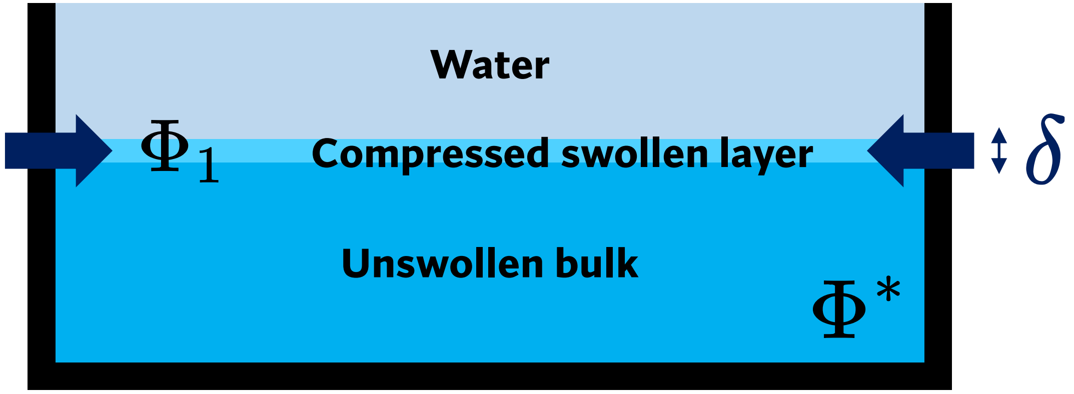

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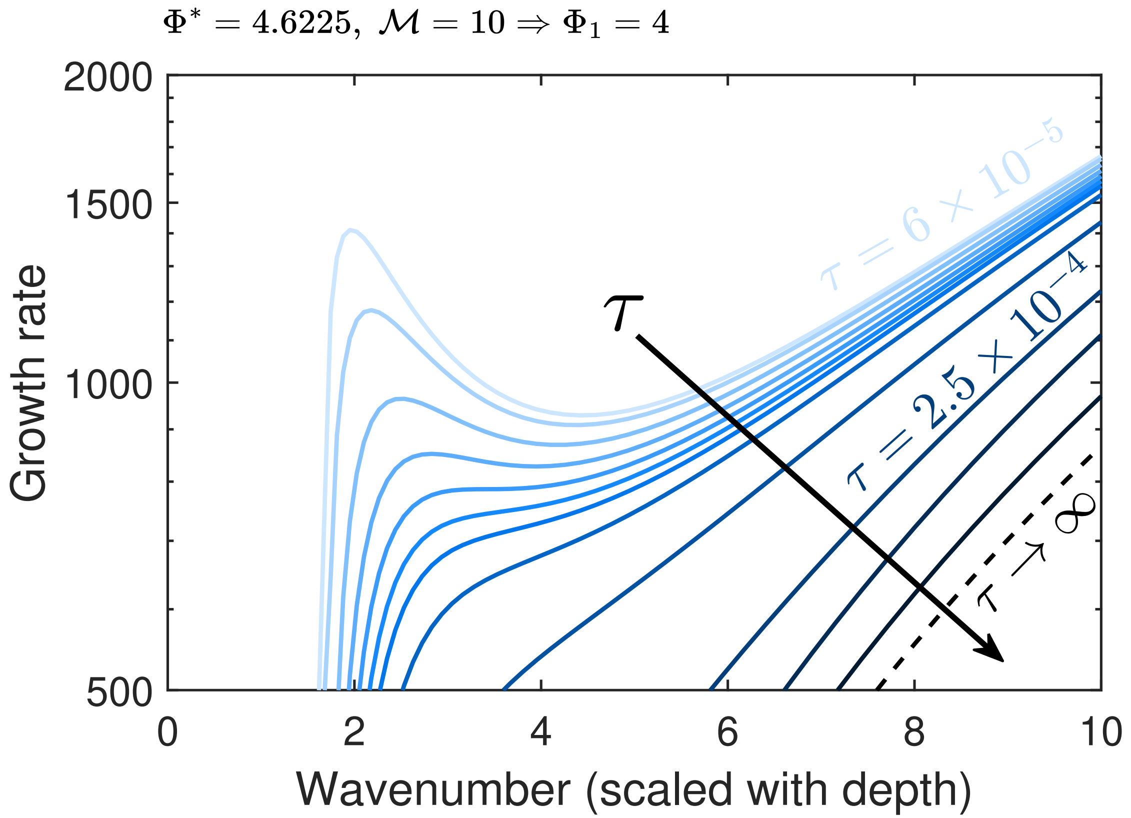
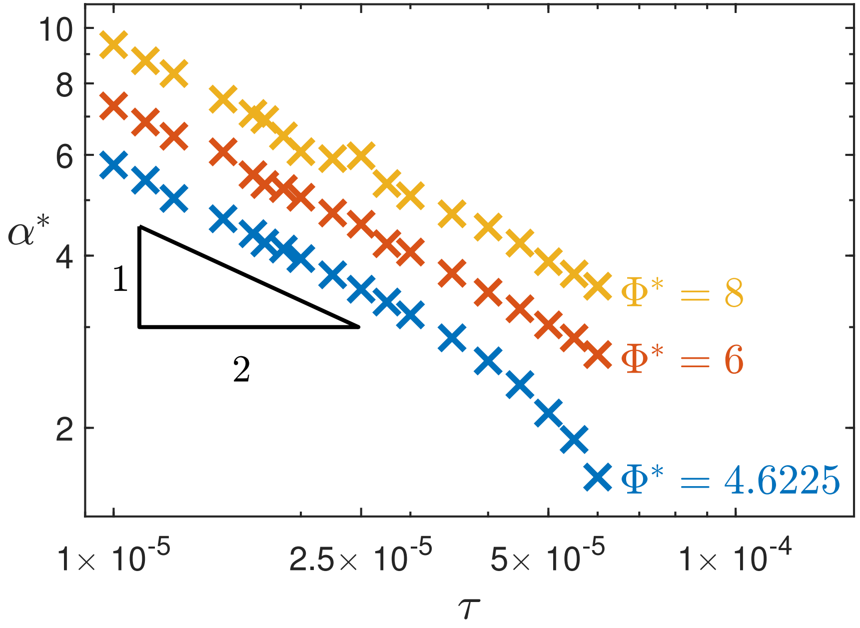


A finite most unstable mode

- *If* the peak is physical, we expect that this is the wavenumber we'll see – no ultraviolet catastrophe here

- Plotting the peak position at $\alpha = \alpha^*$, we see that the wavelength increases with time before the peak disappears, scaling with the thickness δ



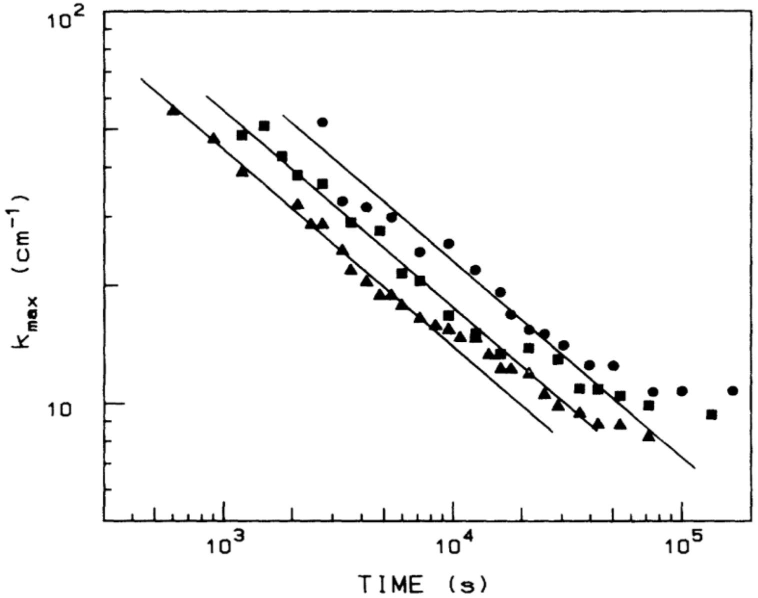
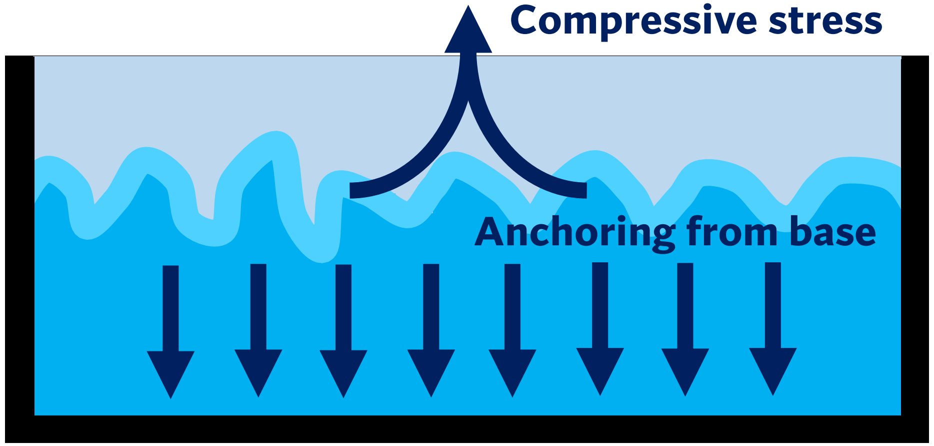


FIG. 4. Temporal change in $k_{\max}$ for the gels I-1–I-3. (●) I-1; (■) I-2; (▲) I-3. All the solid lines have a slope of $-\frac{1}{2}$.

Figure from Tanaka *et al.*, Phys Rev Lett **68**:2794-2798, 1987

- What's the mechanism causing this – can it be captured by our theory?

Buckling instability



- View the base as an elastic incompressible material, bonded to a thin elastic swollen layer
- Classical plate theory gives a balance between stresses to select a finite wavenumber α^* for wrinkles

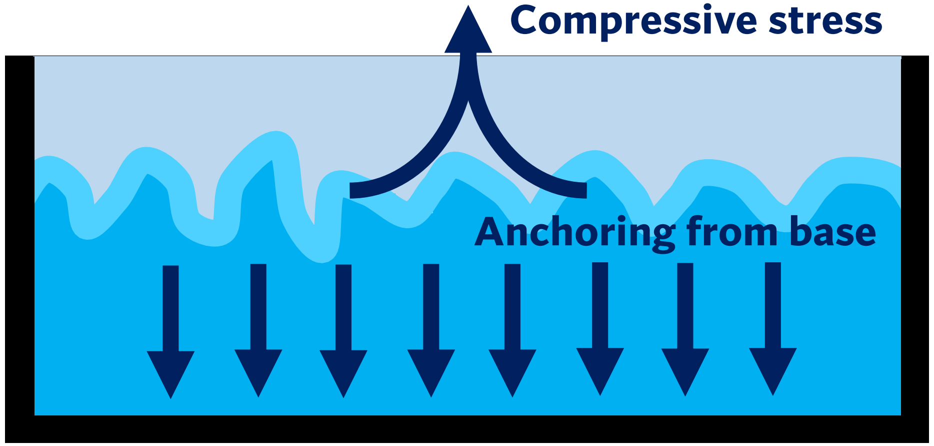
$y = z/a(\tau)$

Interfacial polymer fraction gradient

$$\frac{E\delta^3}{12\left(1-\nu^2\right)}\alpha^4 - 4\mathcal{M}\left(\Phi^{*1/2} - \Phi_1^{1/2}\right)\delta\alpha^2 = -\left[\left(1+\mathcal{M}\Phi^{*-1/2}\right)\Phi_y + \frac{2\mathcal{M}\alpha}{\tanh\left[\alpha(1-\delta)\right]}\right]\cos\left(\alpha x\right).$$

- Look at the dominant balance at early times, when $\delta \ll 1$ alongside $\Phi_y \sim -1/\delta$

Buckling instability



Compressive stress

Anchoring from base

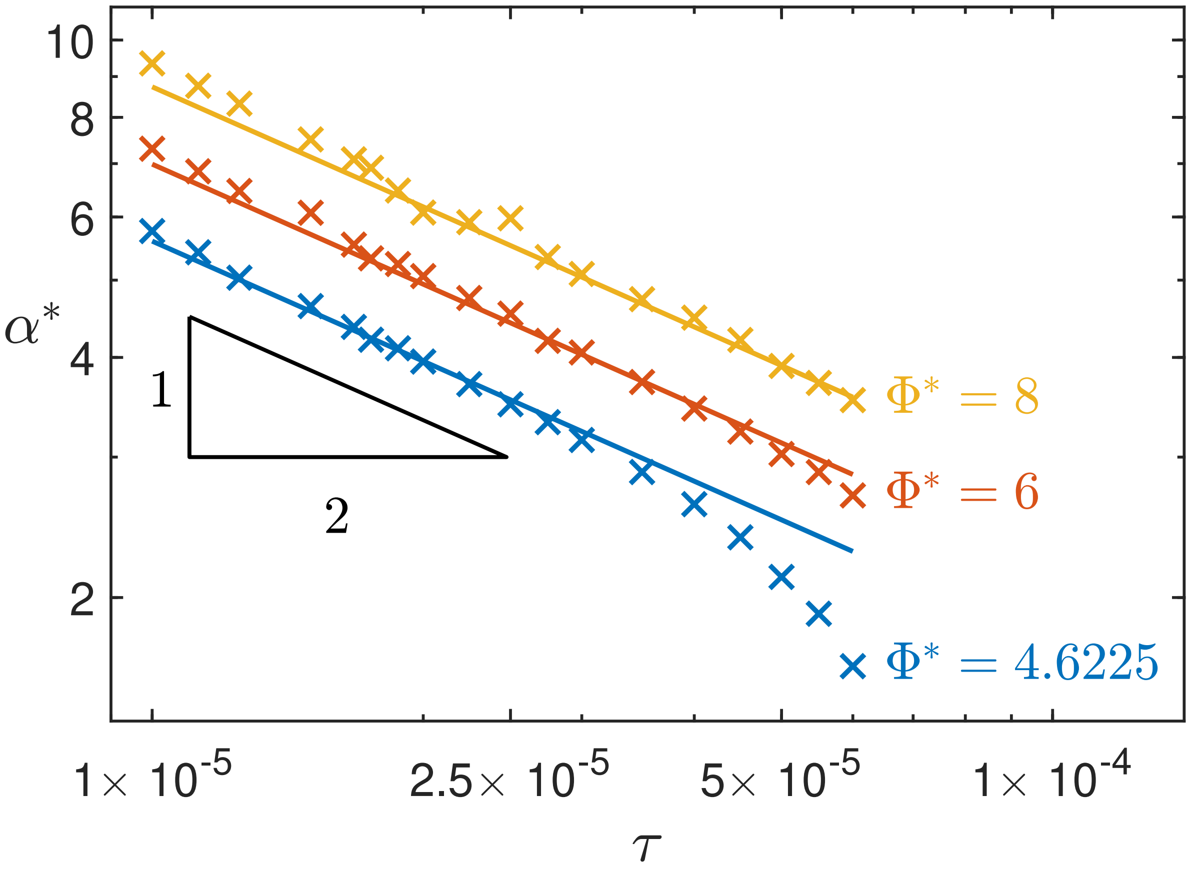
Early-time limit

$$\frac{2\mathcal{M}\alpha^*}{\tanh \alpha^*} = -\left(1+\mathcal{M}{\Phi^*}^{-1/2}\right)\Phi_y$$

$\approx 2\mathcal{M}\alpha^*$

$\propto \tau^{-1/2}$

from similarity solution



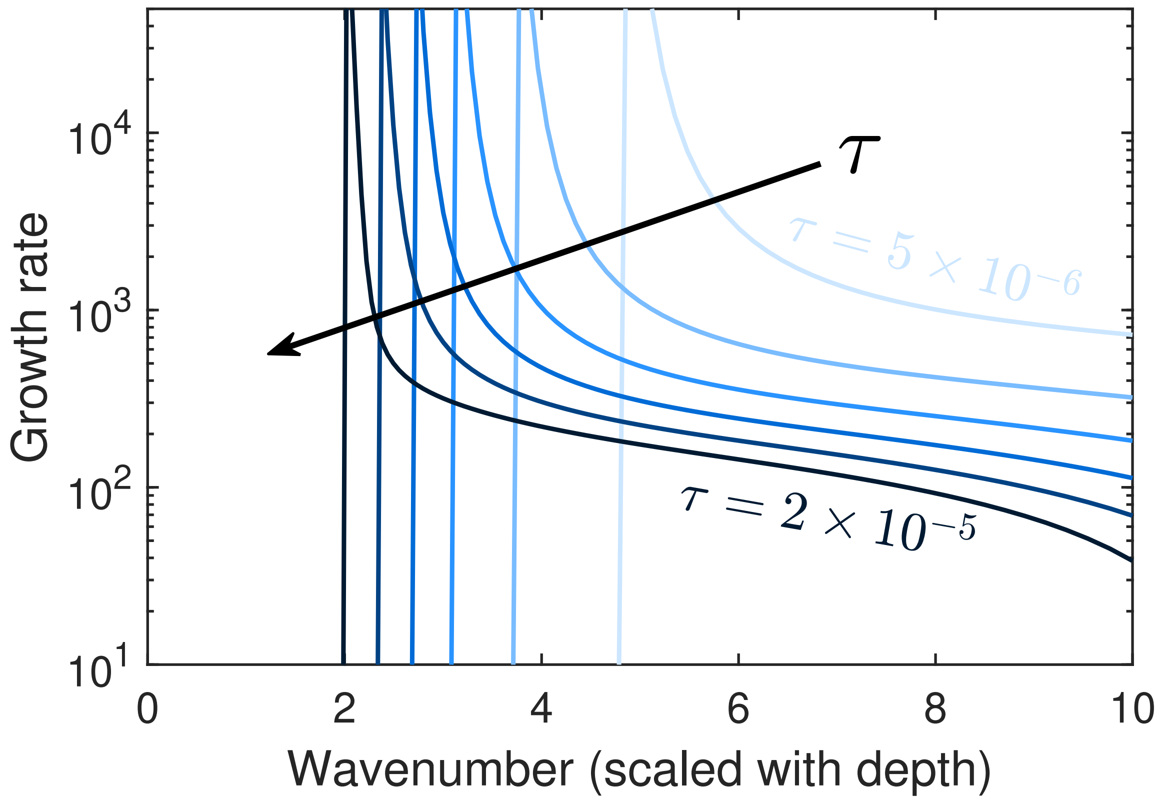
Healing of instabilities

- There is no longer a solution to the equation for buckling if the thickness of the swollen layer is above a critical value

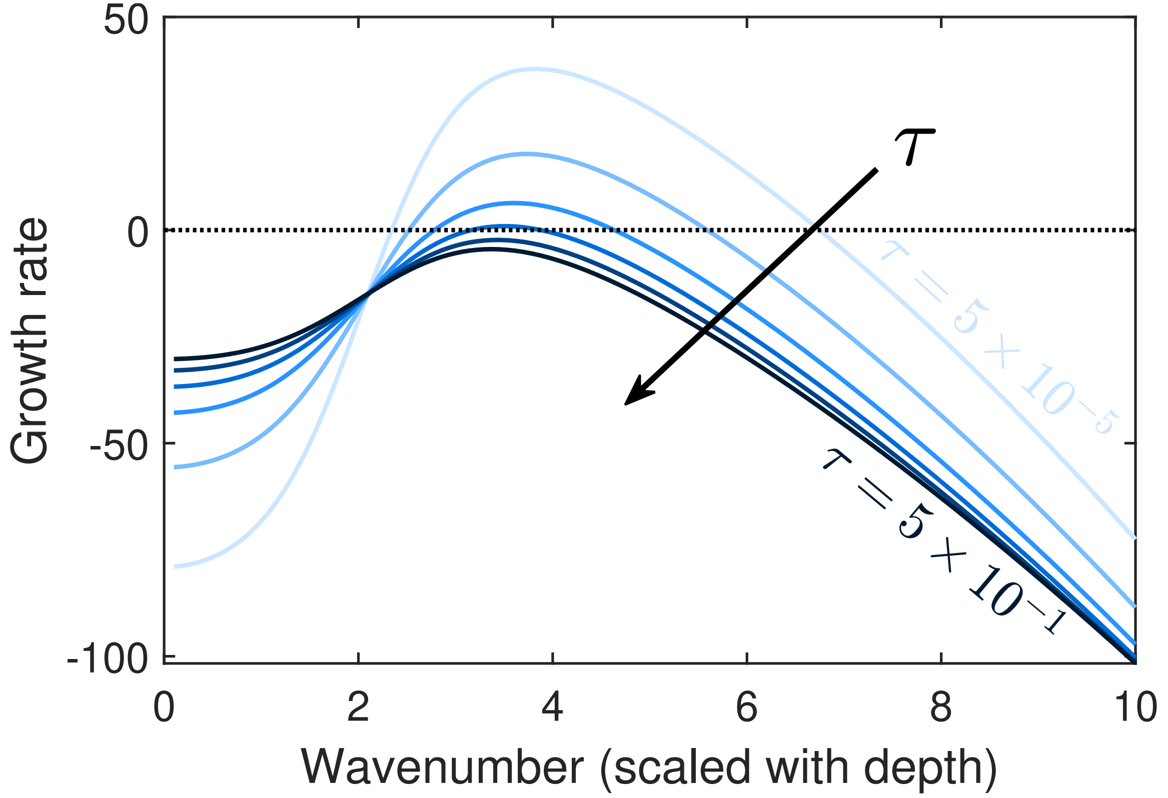
$$\delta_c = \frac{\Phi^* + \mathcal{M}{\Phi^*}^{1/2}}{2\mathcal{M}}\left(1 - \frac{\Phi_1}{\Phi^*}\right)$$

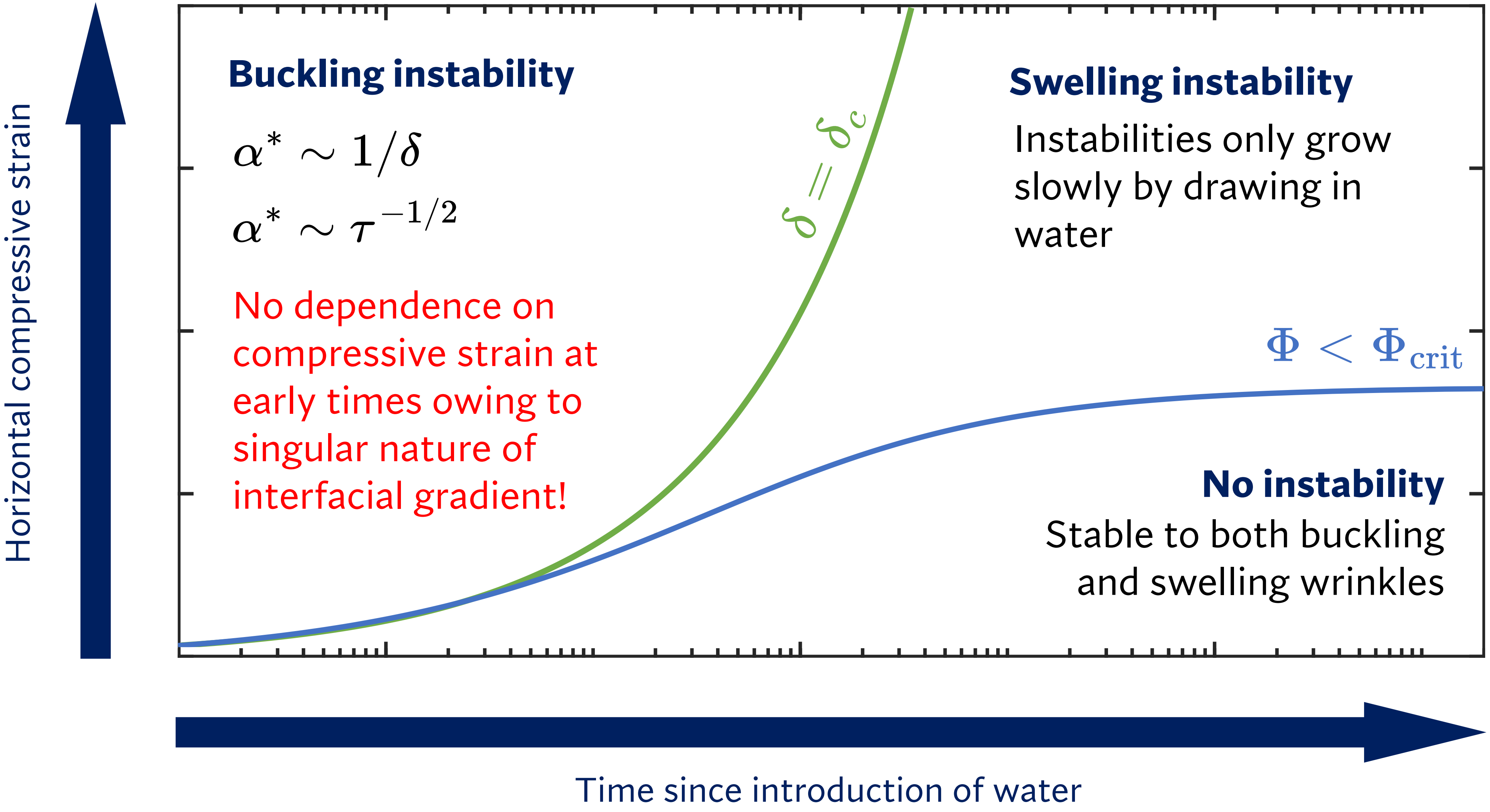
- Here, the effect of the base is too strong and buckling is suppressed
- Thus, we can no longer have a buckling instability
- If we swell to a low enough polymer fraction, we no longer see a swelling instability either, and the wrinkles on the surface ‘heal’

Healing of instabilities



$\Phi^* = 2.75,\ \mathcal{M} = 10 \Rightarrow \Phi_1 < \Phi_{\text{crit}}$





Buckling instability

$$\alpha^* \sim 1/\delta$$

$$\alpha^* \sim \tau^{-1/2}$$

No dependence on compressive strain at early times owing to singular nature of interfacial gradient!

Swelling instability

Instabilities only grow slowly by drawing in water

No instability

Stable to both buckling and swelling wrinkles

Buckling and swelling instabilities of super-absorbent gels

Buckling and swelling instabilities of super-absorbent gels

Webber, J. J. & Worster, M. G. *Wrinkling instabilities of swelling hydrogels* — submitted to PRE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A linear-elastic-nonlinear-swelling theory for hydrogels. Part 1. Modelling of super-absorbent gels

Webber, J. J. & Worster, M. G. *A linear-elastic-nonlinear-swelling theory for hydrogels. Part 1. Modelling of super-absorbent gels*
J. Fluid Mech. **960**:A37 (2023)


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A linear-elastic-nonlinear-swelling theory for hydrogels. Part 2. Displacement formulation

Webber, J. J., Etzold, M. A. & Worster, M. G. *A linear-elastic-nonlinear-swelling theory for hydrogels. Part 2. Displacement formulation*
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