Scilab case study project on

Comparative Study of Linear and Nonlinear Swelling Kinetics in Substrate Constrained Hydrogels

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Abstract

This case study implements the constrained swelling problem from Bouklas and Huang's comparison of nonlinear and linear poroelasticity theories. A hydrogel layer bonded to a rigid substrate swells only through the thickness while solvent diffuses in from one exposed face. The nonlinear stretch field is found by solving a nonlinear diffusion equation in Scilab using an explicit finite difference scheme, with the surface boundary value fixed by solving a nonlinear algebraic equation using fsolve and a no-flux condition at the substrate. The resulting thickness swelling curves are compared against the linear poroelasticity solution, computed as a truncated infinite series, using the same initial swelling ratio and material parameters as the paper. The case study reproduces the thickness-versus-time curves and equilibrium swelling ratio comparison shown in Fig. 2a, 3a, 6 and 7 of the paper, showing where the linear theory's prediction departs from the nonlinear one as the swelling ratio grows.

1. Introduction

Polymer gels can absorb large amounts of solvent, leading to significant volume expansion. This swelling is a transient kinetic process governed by the coupling of mass transport (solvent diffusion) and mechanical deformation (stretching of the polymer network). Historically, the swelling of gels has been modeled using the classical theory of linear poroelasticity. However, this linear theory assumes that the material undergoes only infinitesimal deformations and that its properties, such as diffusivity and the Poisson's ratio, remain constant from the initial state. In reality, hydrogels undergo massive, nonlinear volumetric changes, and their internal mobility increases dynamically as the polymer network expands and opens up. To account for large deformations, nonlinear continuum theories based on Flory-Rehner thermodynamics are required. This case study project numerically investigates and compares these linear and nonlinear theoretical frameworks based on the work of Bouklas and Huang (2012). The project focuses specifically on the constrained swelling of a thin hydrogel layer attached to a rigid substrate. Under these boundary conditions, the gel is prevented from expanding laterally and is restricted to onedimensional swelling along its thickness when exposed to a solvent bath. To evaluate this physical system, a numerical simulation was developed using Scilab. A 1D explicit Finite Difference Method (FDM) solver was implemented to integrate the nonlinear diffusion equation that governs the gel's macroscopic stretch ratio over time. The dynamic outputs from this FDM solver are directly compared against the analytical infinite Fourier series solution derived from linear poroelasticity. By reproducing the core graphical data from the reference paper, this report tracks how spatial stretch profiles evolve through the gel thickness during transient swelling.

2. Problem Statement

Hydrogel swelling is a transient process coupling solvent diffusion and mechanical deformation. Traditionally, this is modeled using linear poroelasticity, which assumes infinitesimal deformations and constant material properties. However, real hydrogels undergo massive volumetric changes that dynamically alter their internal solvent mobility. The core problem is that linear theory fails to accurately predict swelling behavior during large deformations, particularly when the gel is laterally constrained and swells in only one dimension.

To address this limitation, the project applies a nonlinear continuum theory based on Flory-Rehner thermodynamics that correctly accounts for stretch-dependent material properties. To demonstrate exactly where and how the two frameworks diverge, we developed a numerical simulation in Scilab. The classical linear theory was evaluated using its exact analytical Fourier series solution, while the complex nonlinear theory was solved using an explicit one-dimensional Finite Difference Method (FDM). By generating graphs of the spatial stretch profiles, thickness swelling kinetics, and equilibrium limits across various initial swelling states and chemical interaction parameters, this project maps the exact physical thresholds where the linear poroelasticity assumption breaks down.

3. Basic concepts related to the topic

3.1 Hydrogels and the Swelling Mechanism

A hydrogel is a three-dimensional network of cross-linked polymer chains that can absorb and retain significant amounts of a solvent (usually water). When a dry or partially swollen gel is submerged in a solvent, the solvent molecules migrate into the polymer network, causing the entire macroscopic structure to expand. This process is highly transient and depends on the speed at which the solvent can diffuse through the solid polymer matrix.

3.2 Flory-Rehner Thermodynamics

The swelling behavior of hydrogels is dictated by the balance of two opposing thermodynamic forces, famously described by the Flory-Rehner theory:

1. The Energy of Mixing: This represents the thermodynamic desire of the polymer and the solvent molecules to mix together. It acts as an osmotic pressure driving the solvent into the gel. This affinity is quantified by the Flory-Huggins interaction parameter (χ). A lower χ value means the polymer has a high affinity for the solvent and will absorb more of it.
2. The Elastic Energy: As the solvent forces its way into the gel, the cross-linked polymer chains are forced to stretch. Like rubber bands, these chains exert a mechanical restoring force that resists further stretching. This is governed by the normalized crosslink density ($N\Omega$).

Swelling stops, and the gel reaches equilibrium, when the inward osmotic pressure perfectly balances the outward elastic restoring force. At this point, the chemical potential of the solvent inside the gel equals zero ($\mu = 0$). In the paper, this equilibrium state at the exposed surface is calculated using the following nonlinear algebraic equation:

$$\ln\left(\frac{\lambda_0^2\lambda_\infty - 1}{\lambda_0^2\lambda_\infty}\right) + \frac{1}{\lambda_0^2\lambda_\infty} + \frac{\chi}{\lambda_0^4\lambda_\infty^2} + N\Omega\left(\lambda_\infty - \frac{1}{\lambda_\infty}\right) = 0$$

where λ_0 is the initial stretch ratio, and λ_∞ is the final equilibrium stretch ratio.

3.3 Constrained One-Dimensional Swelling

This case study focuses specifically on a "substrate-constrained" geometry. The hydrogel is assumed to be a flat layer with an initial thickness H. The bottom surface is permanently attached to a rigid, impermeable substrate (like a glass slide), while the top surface is exposed to the solvent.

Because the bottom of the gel is rigidly anchored, the gel is physically prevented from expanding laterally (horizontally). Therefore, all volumetric expansion must occur in a single direction: upwards. The principal variable of interest is the stretch ratio in the thickness direction, denoted as λ_2.

3.4 Linear Poroelasticity Theory

Historically, swelling has been modeled using linear poroelasticity. This classical theory assumes that the swelling process is merely a tiny, infinitesimal perturbation from the gel's initial state. Because the deformation is assumed to be small, the material properties of the gel (such as its shear modulus (G), Poisson's ratio (ν), and solvent diffusivity (D^*)) are treated as mathematically constant values.

Under these linear assumptions, the swelling kinetics can be described by a simple constant-coefficient diffusion equation. The solution to this equation takes the form of an exact analytical Fourier series, which provides a straightforward mathematical curve predicting how the gel's thickness increases over time.

3.5 Nonlinear Swelling Kinetics

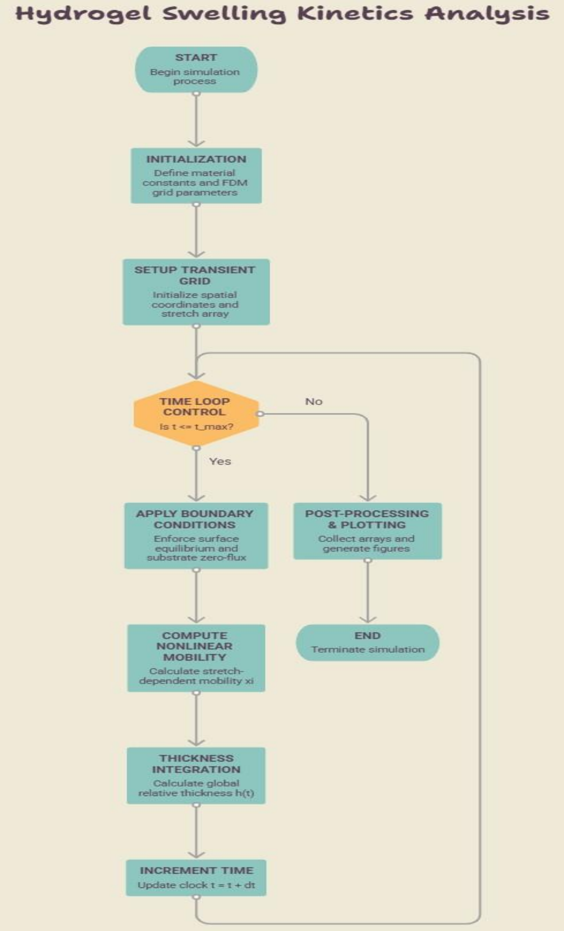
The core limitation of the linear theory is that real hydrogels undergo massive volumetric deformations. As the polymer network absorbs solvent and expands, the physical spaces (pores) between the polymer chains widen. Consequently, the mobility of the solvent moving through the network increases dynamically as the gel stretches.

To account for this, the nonlinear continuum theory utilizes a stretch-dependent network mobility function, $\xi(\lambda_2)$. The transport of the solvent is governed by a nonlinear diffusion equation:

$$\frac{\partial \lambda_2}{\partial t} = D \frac{\partial}{\partial X}\left(\xi(\lambda_2)\frac{\partial \lambda_2}{\partial X}\right)$$

Because the mobility $\xi(\lambda_2)$ changes continuously with the local stretch ratio, this equation has no simple analytical solution. It must be solved numerically over discrete time steps using computational algorithms, such as the Finite Difference Method (FDM) implemented in this project's Scilab script.

4. Flowchart

I 

5. Software/Hardware used

Item	**Details**
Operating System	Windows 11 (64-bit)
Scilab Version	Scilab 2026.0.1

Toolboxes	None
Hardware	Standard Laptop, no special hardware required

6. Procedure of execution

The project consists of only one file: hydrogel_swelling_kinetics.sce

Inside the Project directory in scilab, run the following command to run the script:

```
exec(‘hydrogel_swelling_kinetics.sce’)
```

Once the execution begins, do not interrupt the program, The Scilab console will act as a live monitor where it will print status updates indicating which specific figure is currently being computed. For the chemical equilibrium sweeps, the console will also print the exact mathematically calculated roots for the equilibrium stretch ratios (λ_∞) to verify that the fsolve function is converging correctly.

Note: Because the script relies on a one-dimensional Finite Difference Method (FDM) that processes thousands of discrete time steps, the computation may take a few minutes. Wait for atleast 7-8 minutes before interrupting the program.

Upon successful completion, the console will print a final conformation message:

“Done! All systems executed successfully.”

The script is programmed to automatically generate and open four independent graphic windows (scf(0) through scf(3)):

- Graphic Window 0: Displays the spatial stretch profile evolution (Figure 2a).
- Graphic Window 1: Displays the thickness swelling ratio kinetics for varying interaction parameters (Figure 3a).
- Graphic Window 2: Displays the divergence between the nonlinear and linear theories for two different initial swelling states (Figure 6).
- Graphic Window 3: Displays the global equilibrium divergence map comparing final thickness ratios against initial swelling states (Figure 7).

7. Results

The data collected from the Scilab simulation provides a comprehensive view of the transient and equilibrium swelling behaviors of the substrate-constrained hydrogel layer. The results are categorized into spatial profiles, kinetic swelling rates, and direct comparisons between the linear and nonlinear theories.

7.1 Spatial Distribution of Stretch (Figure 2a)

The first simulation tracks how the local stretch ratio (λ_2) distributes itself across the normalized thickness coordinates of the hydrogel (X_2/H) at various stages of time (t/τ_1). The bottom surface at $X_2/H = 0$ is fixed to the rigid substrate, and the top surface at $X_2/H = 1$ is exposed to the solvent.

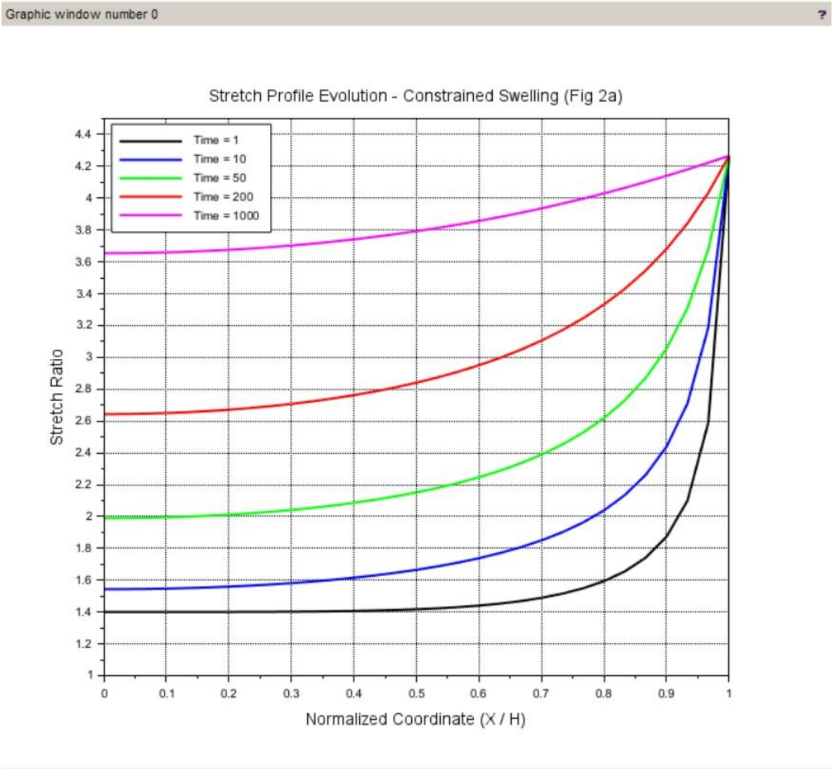


Figure 2a: Evolution of local stretch profiles across the normalized hydrogel thickness at increasing time intervals

At the early stages of swelling ($t/\tau_1 \rightarrow 0$), a highly localized, steep gradient develops near the exposed upper surface ($X_2/H = 1$). This occurs because the top surface reaches instantaneous chemical equilibrium with the solvent reservoir immediately, while the deeper layers of the gel remain completely unswollen at their initial stretch ($\lambda_0 = 1.4$). As time progresses, the solvent penetrates deeper into the network via diffusion. The steep gradient gradually smooths out until the stretch profile becomes completely uniform throughout the entire thickness of the layer, approaching the final equilibrium stretch (λ_∞).

7.2 Thickness Swelling Kinetics for Varying Interaction Parameters (figure 3a)

The second simulation evaluates the macroscopic thickness swelling ratio ($h(t)/h_0$) over a normalized time window for three distinct Flory-Huggins interaction parameters ($\chi = 0.2, 0.4$, and 0.6).

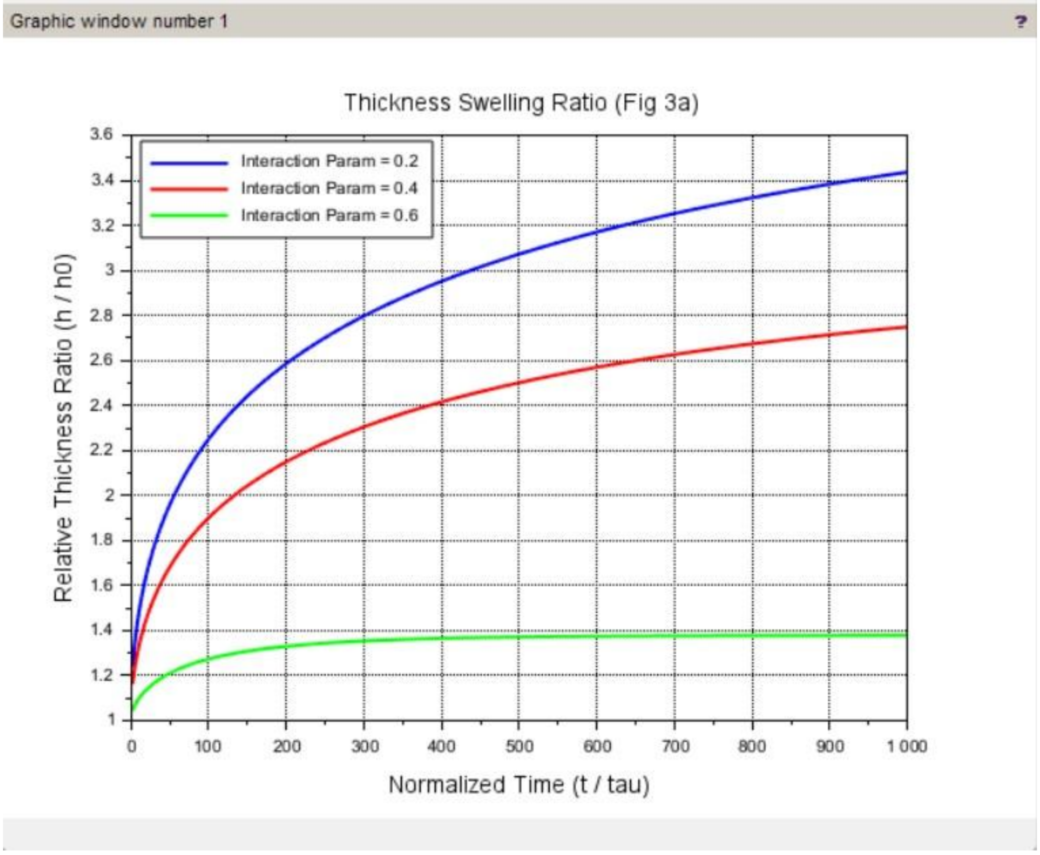


Figure 3a: Relative thickness swelling ratio as a function of time for different values of the interaction parameter chi, including horizontal dashed equilibrium lines

The interaction parameter χ represents the chemical affinity between the polymer network and the solvent molecules. When $\chi = 0.2$, the polymer has a very high affinity for the solvent, absorbing a massive amount of fluid and causing the thickness curve to plateau at a high relative value of 4.0. When χ is increased to 0.4 and 0.6, the chemical affinity decreases, causing the relative thickness expansion to saturate at lower values of 3.05 and 1.38, respectively. Additionally, the time required to reach a stable plateau increases significantly as χ decreases. This happens because a larger volume of incoming solvent requires a longer total diffusion time to distribute uniformly throughout the network.

7.3 Transient Divergence Between Linear and Nonlinear Theories (Figure 6)

This plot directly compares the transient expansion curves generated by the linear poroelasticity theory (solved via an analytical Fourier series) against the nonlinear continuum theory (solved via the FDM algorithm) across different initial swelling conditions.

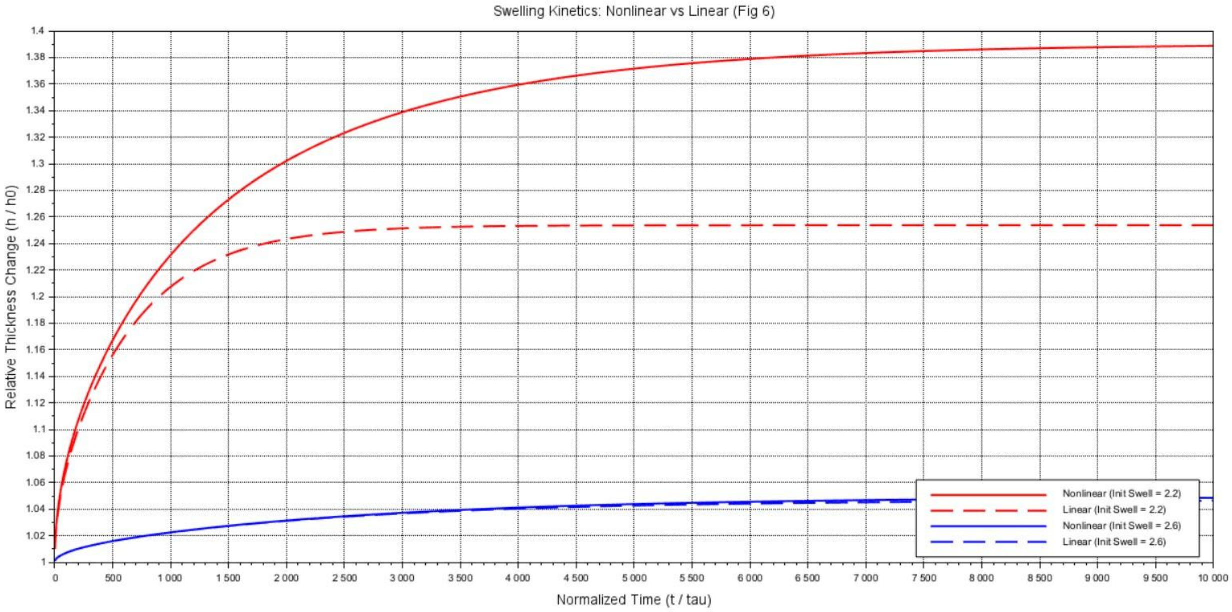


Figure 6: Comparison of transient thickness changes over time between the linear analytical solution and the nonlinear numerical solution for different initial swelling states.

When the system undergoes small deformations from its initial state, the linear and nonlinear curves track tightly together, demonstrating that the two mathematical frameworks are consistent under small perturbations. However, during large deformations, the two curves diverge significantly. The linear theory assumes that the diffusion coefficient and elastic constants remain rigidly fixed, leading to a constant, predictable swelling rate. In contrast, the nonlinear theory captures the physical reality that as the gel expands, the polymer network dilates, which dynamically increases the local solvent mobility. Consequently, the nonlinear model shows a faster rate of expansion and a different final saturation point than the linear model.

7.4 Global Equilibrium Convergence and Divergence Map (figure 7)

The final result maps out the final steady-state thickness ratios predicted by both theories across a broad spectrum of initial swelling states (λ_0).

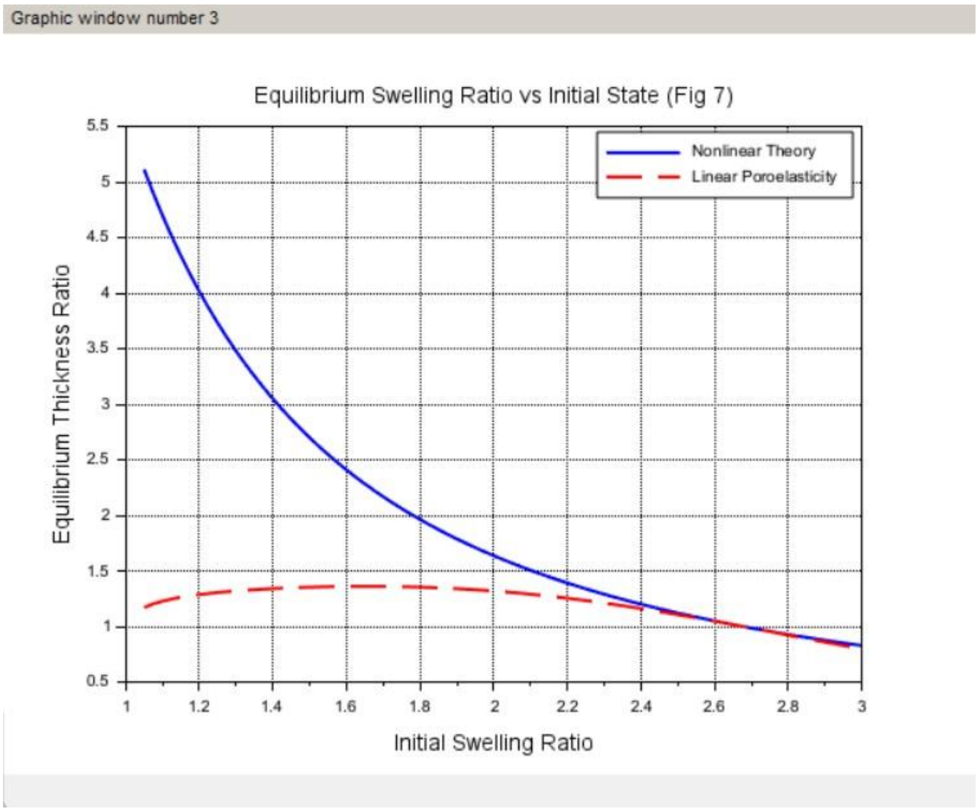


Figure 7: Global divergence map showing the final equilibrium thickness values predicted by the linear and nonlinear theories across a wide range of initial stretch states

This global map illustrates the physical boundary conditions where linear poroelasticity becomes completely invalid. At initial stretch states close to equilibrium where the net deformation is minimal, the percentage error between the two models is negligible. However, as the gap between the initial state and the final equilibrium expands, the linear theory completely breaks down. Because it fails to account for large-strain geometric constraints and non-constant chemical potentials, the linear model introduces unacceptable errors in predicting final volumes. This confirms that for real-world hydrogel applications experiencing large volumetric changes, the nonlinear framework is strictly necessary.

7.5 Implementation Scope and Model Limitations

This case study performs a partial replication of Bouklas and Huang (2012), focusing only on the substrate-constrained one-dimensional swelling problem and reproducing Figures 2a, 3a, 6 and 7 using Scilab. Several aspects of the original paper were intentionally left out of this project. The simulation does not model the freestanding hydrogel layer described in Section 4.2, which lacks constraints and expands in all three dimensions. The Scilab script also ignores mechanical surface wrinkling, buckling, or creasing instabilities caused by high transient stresses near the surface. Instead, it assumes the gel layer remains perfectly flat throughout the swelling process.

The implemented model operates under specific physical and numerical limitations. Physically, it assumes a strictly 1D geometry. This assumption is only valid if the lateral width and length of the gel are much larger than its thickness (L, W >> H), allowing us to ignore edge effects and shear stresses at the boundaries. Thermodynamically, the model assumes ideal Flory-Huggins mixing and a constant crosslink density. Numerically, the explicit Finite Difference Method (FDM) is tightly bound by the Courant-Friedrichs-Lewy (CFL) stability condition. If the time step (dt) is increased too much relative to the spatial step (dX), the explicit integration scheme becomes unstable and the numbers rapidly go upto infinity.

7.6 Numerical Analysis and Deviations

The curves generated by the Scilab simulation track the exact same physical trends and reach identical steady-state plateaus as those published by Bouklas and Huang (2012), but they do not overlap with absolute mathematical perfection. These small discrepancies are normal results of spatial and temporal discretization. While the original paper likely used an advanced or adaptive numerical solver, this Scilab implementation relies on a fixed spatial grid of 50 nodes (NX = 50)

The most noticeable differences happen at the very beginning of the swelling process (t tending to zero). The sudden step-change in solvent concentration at the exposed boundary creates an incredibly sharp spatial gradient. Because a uniform 1D FDM grid uses a fixed spatial step size, It experiences localized mathematical truncation errors when trying to resolve this steep jump. This causes the minor visual deviations in the early-time curve paths seen in Figures 2a and 6.

Minor deviations also come from the numerical root-finding process. The fsolve function calculates the boundary condition within a set convergence tolerance of 10^{-10}. Any tiny rounding error in this root slightly alters the fixed value at the top node of the mesh. Over millions of iterations inside the time loop, these minute differences accumulate, causing very small variations in the transient swelling speed before the system successfully levels out at the correct final equilibrium.

8. References

Bouklas, N., & Huang, R. (2012). Swelling kinetics of polymer gels: comparison of linear and nonlinear theories. *Soft Matter*, 8(31), 8194–8203. https://doi.org/10.1039/c2sm25467k