



Shrinking and Swelling Dynamics in 1D Thermo-Reponsive Hydrogels



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Abstract

Thermo-responsive hydrogels (TRHs) are polymer networks that, when submerged in fluid, respond to changes in temperature by spontaneously absorbing or expelling fluid, in the process changing their volume by a factor of up to 1000. Previous experimental and theoretical studies have considered the dynamics of swelling and shrinking in scenarios where the temperature is changed uniformly throughout the TRH-solvent system. We consider a hypothetical one-dimensional TRH, and after re-deriving the model appropriate for studying uniform temperature changes, we derive the equations of motion governing shrinking and swelling in general stationary temperature distributions. Although we don't solve these equations, we find an additional thermal forcing term proportional to the temperature gradient, that will ultimately play a role in more exotic scenarios with temperature fields dependent on time.

1 Introduction

Gels are elastic materials with the ability to absorb large amounts of fluid, increasing their volume by a factor of up to 1000 times their size (Ilavsky et al. [Ila+81]). Although certain gels can be made from colloidal solutions - yoghurt being one such example - most gels are comprised of large polymer networks, formed by creating cross-links between individual polymer chains. Interestingly, in certain gels, the extent of swelling can depend on external conditions and certain changes in external conditions will induce the spontaneous expulsion of absorption of solvent. Changes in stimuli such as pH and solvent composition (Tanaka et al. [Tan+80]), and in the case of certain ionic gels, the local electric field (Tanaka et al. [Tan+82]) have been found to induce large changes in equilibrium volume in polymer gels. In this report however, we focus on gels that respond to changes in temperature; namely thermo-responsive hydrogels (TRHs). For example, poly(N-isopropylacrylamide) — PNIPAM — gels have been observed to spontaneously switch from hydrophilia to hydrophobia, suddenly collapsing as their temperature is increased above specific transition temperatures (Sato Matsuo and Tanaka [ST88]) - a process referred to as a discontinuous volume-phase transition. Taking the case of Sato Matsuo and Tanaka [ST88]'s study as a representative example, the temperature range within which volume-phase transitions took place was found to be $\sim 34\text{-}60^\circ\text{C}$, depending on the polymer network's degree of ionisation. Crucially, these temperatures are not only experimentally achievable, but biologically relevant, and as such, the possible applications of TRHs are wide and varied, from grippers in soft robots (Li et al. [Li+17]), to controllable drug-release vessels (Sood et al. [Soo+16]).

Experiments studying the kinetics of shrinking and swelling have mainly focused on how gels respond to abrupt changes in the temperature of the solvent bath they sit in, typically by quickly switching the temperatures set by temperature regulators connected to the gel-solvent container (Sato Matsuo and Tanaka [ST88]). As such, new thermal equilibrium can be achieved almost instantaneously when compared with the time for the gel to reach its new equilibrium size.

Theoretical attempts to model the shrinking and swelling dynamics of TRHs have also mainly focused on this situation, where the assumption is made that thermal equilibrium between the gel, solvent and an external heat bath is attained instantaneously (Butler2022; Tomari and Doi [TD95]). In general, however there will be some transient effects as the temperature in the system reaches steady state, as governed by the heat equation. In addition, and to the best of this author's knowledge, no attempts have been made, experimentally or theoretically, to study TRHs in driven systems, where a source periodically pumps heat into the gel, or in systems with non-zero temperature gradient, both of which will be relevant in biomedical settings: the human body, for example, is certainly not in uniform thermal equilibrium. As such, it remains unclear what novel dynamics might be uncovered in these scenarios, and how these might affect the design of new TRH technologies.

Therefore, in this report, we work towards deriving the equations of motion for a thermo-responsive hydrogel experiencing a general, stationary temperature distribution. In addition, to simplify the resulting mathematics, we consider a hypothetical one-dimensional gel that is restricted in the y and z directions, and is only allowed to deform along the x-axis.

Before working up to general temperature distributions, we start in §2.1 by introducing the mathematics required to describe deformations in a gel, before specifying the free energy of a gel experiencing a general deformation in a uniform temperature field. This allows us to derive the equilibrium behaviour of our 1D TRH in §2.4, followed by the force balance in a freely swelling gel in section §2.5.

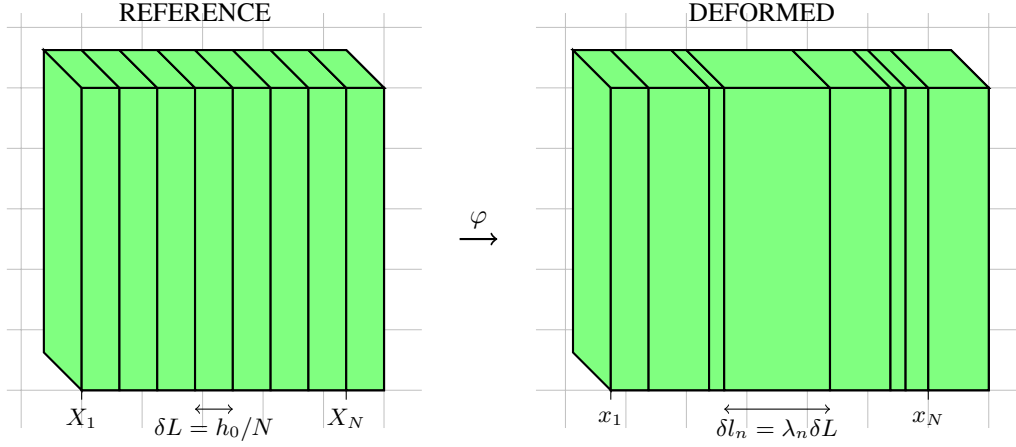


Figure 1: Illustration of an inhomogeneous 1D deformation from a reference state, where the distances between material points in the gel are stretched and compressed by different amounts along the gel's length. The gel is split N thin slices, where the deformation within each slice is approximately homogeneous, with width's given by: $\delta l_n \approx \partial\varphi/\partial X|_{X_i} \delta L = \lambda_i \delta L$.

Adopting the poro-elastic model of (Bertrand et al. [Ber+16]), we derive an equation governing the time evolution of the gel before solving the resulting partial differential equations using a finite differences scheme, where we highlight and explain the differences between shrinking and swelling. Finally, in §3, we present our theory for the dynamics of a 1D TRH in a general, time-independent, temperature distribution.

2 Uniform Temperature Distributions

2.1 Deformation of a 1D Hydrogel

Consider a transformation where a rectangular gel of length h_0 and cross-sectional area A is deformed from a starting 'reference' state to a new 'deformed' state. An illustration of a general deformation is shown in Figure 1, where the gel is stretched by varying degrees along its length. To describe this transformation, let's follow the positions of material points in the gel's body. Since we will be considering deformations restricted to a single dimension, (the y- and z-coordinates of the material points are fixed), we label the positions of the material points in the reference state by X , and in the deformed state by x . Note that the cross-sectional area of our gel A will be fixed throughout.

In general, the mapping of material points from the reference state to the deformed state will be some arbitrary monotonic (and hence invertible) function, $x = \varphi(X)$, which allows for varying degrees of shrinking/swelling along the gel's length. Despite the potential for high complexity in this deformation, on a small enough scale, local deformations will be linear: labelling the infinitesimal separation (along the x-axis) between two neighbouring points in the reference state by dX , the x-separation between the same two points in the deformed state will be:

$$dx = \left. \frac{\partial\varphi}{\partial X} \right|_X dX = \lambda(X) dX, \quad (1)$$

where $\lambda(X)$ is the local deformation gradient for reference point X ¹. The 1D local deformation gradient also serves the purpose of describing the *local stretch* at reference point X : all distances between points in the vicinity of X are stretched by factor $\lambda(X)$. For a general, inhomogeneous mapping, λ will vary along the length of the gel, $\lambda = \lambda(X)$, and with knowledge of this function, we fully specify the deformation.

To aid our description of the gel's state, we slice the undeformed gel into N discrete slices of each width: $\delta L = \frac{h_0}{N}$. Each slice is then referred to by the positions of the material points coinciding with each slice's left-hand-side, which in the reference state are $\{X_i\}$, with $i = 1, 2, \dots, N$: for example, the positions of the left-hand-walls for the first, last and i^{th} slices are respectively $X_1 = 0$, $X_N = (N-1)\delta L$ and $X_i = (i-1)\delta L$. Then, when the gel is deformed, the slices are mapped to new positions, $x_i = \varphi(X_i)$. The widths of the slices will also be affected and so, inspired by equation (1), we write the width of the i^{th} slice as:

$$\delta l_i \approx \left. \frac{\partial\varphi}{\partial X} \right|_{X_i} \delta L = \lambda_i \delta L. \quad (2)$$

¹For general 3D deformations, this is replaced by $dx = F dX$, where $F = \partial \mathbf{x} / \partial \mathbf{X}$ is the deformation gradient tensor.

This is just a first order approximation for the width, and in general, such an approximation will be quite poor when the number of slices is relatively small, since λ may vary appreciably over each slice. However as the number of slices increases, and δl approaches zero, each slice will experience increasingly uniform stretches and this expression, like equation (1), will become an exact equality when the gel becomes a continuum.

2.2 Free Energy of a Slice

Now, we ask, what is the total free energy of the entire gel, when it experiences a general deformation with stretch $\lambda(X)$? To answer this question, let's focus on the i^{th} slice of gel, which we take to be experiencing stretch, λ_i and sitting at temperature T_i . If we calculate the free energy of this slice, then by summing over all slices and taking the limit $N \rightarrow \infty$, we'll obtain an expression for the total free energy of a gel experiencing any general deformation. Let's also assume that gel is at uniform, constant temperature; eventually we'll want to consider how general temperature distributions affect the gel, but we delay these considerations until section 3. Up until then, we take the temperature of the gel to be T , a constant that can be varied through, for example, the introduction of a new heat-bath.

To calculate the free energy of the i^{th} slice, F_i , we note that the gel system is comprised of two components: a) a polymer network, which provides a porous medium through which b) a solvent, may permeate. The polymer network contains many polymer strands - chains of connected monomers - that are joined at cross-linking junctions. Gels are distinct to regular polymer solutions, in that during the gelation reaction (where gels are formed), cross-linking agents act to connect separate polymer chains, creating a single, very large, macromolecule. We refer to this structure as the polymer network. For what follows, we drop the subscript i , since all quantities discussed in the next sub-section refer to quantities belonging to the i^{th} slice. We then make the following assumptions:

1. The polymer network is composed of a rubber-like, incompressible elastic material, with an evenly distributed number of polymer strands through the network in the reference state, and
2. The density of cross-links in the network is negligibly small.
3. The polymer network experiences *affine deformations*. That is, we assume that each polymer strand in the network stretches in the same way as the gel as a whole,
4. Each network strand contains exactly \mathcal{N} monomers,
5. The solvent is distributed uniformly through any region with constant stretch.

Assumptions 1 and 2 both play important roles in the model for a gel, so before specifying the form for the free energy, we make some observations: Firstly, since the volume of the polymer network is fixed, the gel can only change its volume by absorbing or expelling fluid. As such, the volume of the gel slice at any moment, v may be expressed as:

$$v = v_p + v_f = \Omega_m n_m + \Omega_c n_c + \Omega_f n_f, \quad (3)$$

where in the second equality Ω_m , Ω_c and Ω_f refer to the volumes of one monomer, one cross-linker and one fluid molecule respectively, and n_m , n_c and n_f reference the number of each of these in the given slice. Assumption 2 allows us to neglect the cross-linking agents, so that the total volume of the polymer network in the slice is simply $v_p = \Omega_m n_m$.

Secondly, we define two other useful quantities for describing slice deformations: the polymer and fluid fractions, ϕ_p and ϕ_f , defined as the fraction of volume in a slice occupied by polymer and fluid respectively:

$$\phi_p = \frac{v_p}{v}, \quad \phi_f = \frac{v_f}{v} \implies \phi_p + \phi_f = \frac{v_p + v_f}{v} = 1. \quad (4)$$

Then, following from assumption 5, we may recast these quantities in terms of the stretch acting on the slice by considering the reference state of the gel to be a solid, completely dry block of polymer. The polymer fraction in the reference state is then equal to unity:

$$\phi_p^0 = 1 = \frac{v_p}{v_0} \implies v_p = v_0, \quad (5)$$

such that, when the gel slice swells changing it's volume from $v_0 \rightarrow v = A\delta l = A\delta L\lambda = \lambda v_0$, the polymer and fluid fractions for the slice are:

$$\phi_p = \frac{1}{\lambda}, \quad \phi_f = 1 - \frac{1}{\lambda}. \quad (6)$$

We now specify the functional form for the free energy of the gel slice. Following from assumption 2, the free energy of the slice after the deformation is separable into three additive components:

$$F = F^0 + F^{\text{elast}} + F^{\text{mix}}, \quad (7)$$

where F^0 is the total free energy of the slice before the deformation (a constant, which can safely be set to zero), F^{elast} is the free energy change associated with the deformation of the underlying polymer network and F^{mix} is the free energy change associated with the mixing of the polymer and the solvent. This assumption forms the basis for the Flory-Rehner model for a gel (Flory and Rehner Jr [FR43]). Then, following assumptions 1, 3 and 4, the elastic free energy due to the deformation of the polymer network enclosed by the gel slice can be written as (Rubinstein and Colby [RC03]):

$$F^{\text{elast}} = n_{\text{str}} \frac{k_B T}{2} (\lambda^2 - 1), \quad (8)$$

where n_{str} is the total number of network strands enclosed in the slice - a quantity that is fixed during the deformation - and k_B is Boltzmann's constant. We note that the combination $n_{\text{str}} k_B T$ acts as the shear modulus for the gel. If each network strand contains \mathcal{N} monomers, then the total number of strands $n_{\text{str}} = n_m / \mathcal{N} = n_m \Omega_m / (\mathcal{N} \Omega_m) = v_p / \Omega_{\text{str}} = v_0 / \Omega_{\text{str}}$, where Ω_{str} is the volume occupied by a single network strand made up of \mathcal{N} monomers.

Then, following from assumptions 2 and 5, the mixing free energy may be derived from the Flory-Huggins theory for polymer solutions (Flory [Flo41], Huggins [Hug41], Dimitriyev et al. [Dim+19]). Neglecting the term suppressed by the total number of solvent molecules and monomer units in the gel, this can be written as:

$$F^{\text{mix}} = (n_m + n_f) k_B T [(1 - \phi_p) \ln(1 - \phi_p) + \chi \phi_p (1 - \phi_p)], \quad (9)$$

where the first term in the square brackets represents the configurational entropy of arranging the fluid molecules in the gel slice and the second term (involving χ) represents the enthalpy of mixing. By considering χ to be a function of temperature, $\chi = \chi(T)$, we incorporate thermo-responsive behaviour into our model for a hydrogel. If temperature changes and χ increases, the gel will gain free energy through the mixing term, and so the gel will attempt to reduce its elastic free energy by shrinking, whilst if χ decreases, the mixing free energy will decrease, and the gel will tend to swell. We use the simplest expression for $\chi(T)$ by considering a linear dependence on temperature:

$$\chi(T) = a + bT, \quad (10)$$

where the parameters a and b are constants, whose values can be found by fitting to experimental data.

To cast F^{mix} as a function of the stretch only, and hence obtain the full expression for the free energy of the slice, we first use eqn. 6 to replace all occurrences of the polymer fraction:

$$F^{\text{mix}} = (n_m + n_f) k_B T \left[\left(1 - \frac{1}{\lambda}\right) \ln \left(1 - \frac{1}{\lambda}\right) + \frac{\chi(T)}{\lambda} \left(1 - \frac{1}{\lambda}\right) \right],$$

and then re-express the numbers of monomers and fluid molecules in the slice in terms of volumes and stretch:

$$n_f = \frac{v_f}{\Omega_f} = \phi_f \frac{v}{\Omega_f} = (1 - 1/\lambda) \frac{\lambda v_0}{\Omega_f} = \frac{v_0}{\Omega_f} (\lambda - 1), \quad (11)$$

and similarly for the constant number of monomers in the slice, $n_m = v_p / \Omega_m = v_0 / \Omega_m$. We then make one further simplifying assumption:

6. The volumes of single monomer and fluid molecules are equal: $\Omega_m = \Omega_f$.

Finally, reintroducing subscript i , the total free energy of the i^{th} slice at temperature T and experiencing stretch λ_i is expressed as:

$$F_i = F(T, \lambda_i) = v_0 k_B T \left(\frac{1}{2\Omega_{\text{str}}} (\lambda_i^2 - 1) + \frac{1}{\Omega_f} \left[(\lambda_i - 1) \ln \left(1 - \frac{1}{\lambda_i}\right) + \chi(T) \left(1 - \frac{1}{\lambda_i}\right) \right] \right). \quad (12)$$

2.3 Total Free Energy of a Gel

Now that we have an expression for the free energy of the i^{th} slice, we can calculate the total free energy of the entire gel, at uniform temperature T , by summing over the slices with their respective stretches:

$$\mathcal{F}_{\text{gel}} = \sum_{i=1}^N F(T, \lambda_i) = \sum_{i=1}^N \frac{F(T, \lambda_i)}{v_0} v_0 = \sum_{i=1}^N W(T, \lambda_i) A \delta L = A \sum_{i=1}^N W_i \frac{h_0}{N}, \quad (13)$$

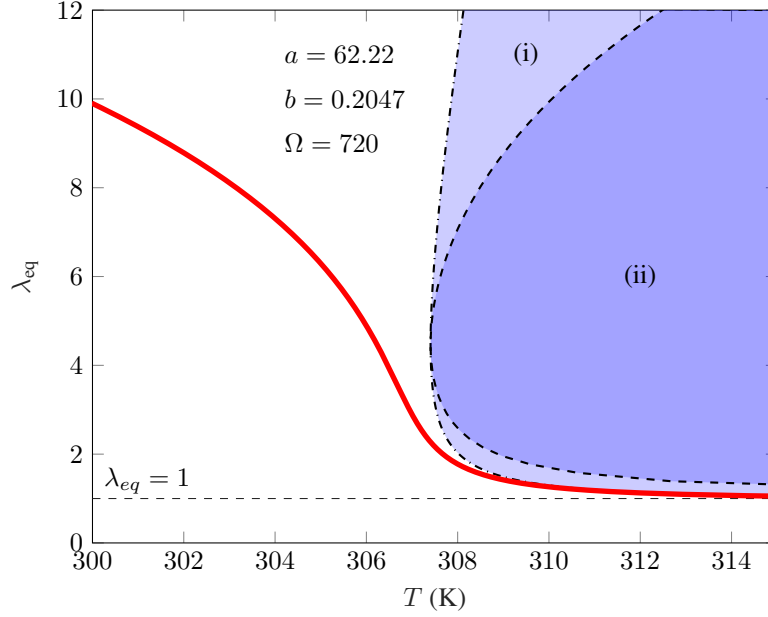


Figure 2: (T, λ) phase-space showing the equilibrium swelling (red, solid line) in free-swelling TRHs as a function of the uniform temperature, T . The shaded regions are (i) the coexistence region and (ii) the spinodal region.

where $W_i = F_i/v_0 = F(T, \lambda_i)/v_0$ is the free energy density of the i^{th} slice. This particular energy density is measured with respect to the reference state volume of a slice, v_0 . Up until the end of this section, we drop the argument T when referring to the free energy, since it acts more as an external parameter rather than a variable.

This is nothing but a Riemann sum, which as the number of slices $N \rightarrow \infty$, becomes an integral over the gel's length:

$$\mathcal{F}_{\text{gel}} = \lim_{N \rightarrow \infty} A \sum_{i=1}^N W_i \frac{h_0}{N} = A \int_0^{h_0} W(\lambda(X)) dX. \quad (14)$$

Here, whilst taking the limit, we have replaced the set of free energy densities, $\{W_i\}$ with the continuous function W , which depends on position through the function $\lambda(X)$.

Now, rather than working with the stretch experienced in the vicinity of material points labelled by their reference coordinate, X , we choose to measure the stretch at fixed points in space: x . To do this, we simply perform the change in variables $x = \varphi(X)$ such that $dx = \lambda dX$:

$$\mathcal{F}_{\text{gel}} = A \int_{\varphi(0)}^{\varphi(h_0)} \frac{W}{\lambda} dx = A \int_{\varphi(0)}^{\varphi(h_0)} w(\lambda(x)) dx, \quad (15)$$

where w is also a free energy density, now measured with respect to current volumes. This can be seen by considering the free energy of the i^{th} slice: it's correct that $F_i = W_i v_0$, yet it is also true to say that $F_i = w_i v_n = w_i \lambda_i v_0$, i.e. the two energy densities are related by $W_i = w_i \lambda_i$. The same holds for the continuous analogy: $W = w \lambda$.

We now have a means for calculating the total free energy of a gel at uniform temperature T , and experiencing general stretch, $\lambda(x)$. This allows us to do two things: a) derive the equilibrium stretch for a gel by minimising its free energy with respect to λ at different temperatures and b) write down the force balance for the gel which, in section 2.7 allows us to derive the dynamical equation for the time evolution of the gel.

2.4 Equilibrium States

When the temperature of the gel is constant and uniform, we expect swelling in the equilibrium state to be homogeneous, since every point in the gel is equivalent. Therefore, the stretch should be uniform throughout the gel at equilibrium: $\lambda(x) = \lambda_{eq}$, so the free energy of the gel at equilibrium is given by:

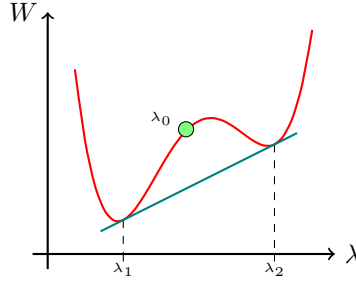


Figure 3: Sketch of the free energy density as a function of stretch, at a temperature where coexistence will occur. A gel forced into state with stretch λ_0 will phase-separate into two regions of different stretches: λ_1 and λ_2 , where the requirement that the two regions are in equilibrium, and minimise the total energy of the gel, is given by the common tangent construction.

$$\mathcal{F}_{\text{gel}} = AW(\lambda_{eq}) \int_0^{h_0} dX = Ah_0 W(\lambda_{eq}) = V_0 W(\lambda_{eq}). \quad (16)$$

Equilibrium is attained by the λ_{eq} for which \mathcal{F}_{gel} is extremised, and since V_0 is a constant (equal to the total volume of the gel in the reference state), the equilibrium condition is simply:

$$\left. \frac{dW}{d\lambda} \right|_{\lambda_{eq}} = 0. \quad (17)$$

Substituting in equation (12), differentiating and dividing by the volume of a single fluid molecule, we find the following non-linear equation for the stretch:

$$\frac{\lambda_{eq}}{\Omega} + \ln \left(1 - \frac{1}{\lambda_{eq}} \right) + \frac{1}{\lambda_{eq}} + \frac{\chi(T)}{\lambda_{eq}^2} = 0, \quad (18)$$

where we define the dimensionless parameter $\Omega = \Omega_{str}/\Omega_f$, which like a and b , can be treated as parameter determined by fitting to experimental data. We do this because the average network strand lengths - and hence network strand volumes - depend on the concentration of cross-linking agents in the polymerisation reaction during gelation - a quantity that varies from gel-to-gel. Therefore we prefer to find these values through fitting to a specific samples of hydrogel, rather than derive expressions for their values. Typical values for Ω are of the order $10^2 - 10^3$ (**Butler20XX**, Bertrand et al. [Ber+16]).

Figure 2 shows a plot of the equilibrium stretches, λ_{eq} as a function of temperature of the gel, T for a particular choice of parameters, a, b, Ω . The plot illustrates a sudden increase in equilibrium size as temperature is reduced below a threshold temperature (about 308 K in this instance), reproducing the characteristic behaviour observed in the equilibrium radius of spherical PNIPAM gels at different temperatures (Sato Matsuo and Tanaka [ST88]).

Figure 2 also includes two shaded regions relevant to the phenomenon of phase-separation, a process observed experimentally in spherical gel beads: when heated above their transition temperature, beads forms an outer shell of shrunken gel that encloses inner, swollen gel. The interface between the two phases then propagates inwards, shrinking in the process (Sato Matsuo and Tanaka [ST88]). Modelling from **Butler2022**; Sekimoto [Sek93], Sato Matsuo and Tanaka [ST88], and Hennessy, Münch, and Wagner [HMW20] accounts for the phase separation that occurs during shrinking by considering the form of the free energy in the (T, λ) phase-space. We start with the spinodal region, labelled (ii) in Fig. 2. This region of phase space is characterised by convex free energy:

$$\frac{\partial^2 W(T, \lambda)}{\partial \lambda^2} \leq 0, \quad (19)$$

As such, configurations of gel within this region are completely unstable, and will cause points throughout the gels volume to spontaneously swell or shrink. This is called spinodal decomposition.

The second relevant region in Figure 2 is the coexistence region, labelled (i), where the form of the free energy is such that the gel can reduce it's total energy by separating into two adjacent regions with different degrees of swelling. This is possible when the gel is forced into a configuration where it's free energy has two local minima separated by a local maximum. An illustration of this is shown in Figure 3. If the temperature is changed and the gel ends up somewhere on the local maximum, it will phase separate into two regions of different stretches, λ_1 and λ_2 . The requirement that the two regions are in mechanical and thermodynamic equilibrium with one another, and that the total energy of the entire gel is minimised by the phase separating, is given by the common tangent construction (Sekimoto [Sek93]):

	Mapping φ	Mapping φ'	Change
Position	$x_i = \varphi(X_i)$	$x'_i = \varphi'(X_i) = x_i + \delta u(x_i)$	$x'_i - x_i = \delta u(x_i)$
Stretch	$\lambda_i = \frac{\partial \varphi}{\partial X} \Big _{X_i}$	$\lambda'_i = \frac{\partial \varphi'}{\partial X} \Big _{X_i} = \lambda_i + \lambda_i \frac{\partial \delta u}{\partial x} \Big _{x_i} \dagger$	$\delta \lambda_i = \lambda_i \frac{\partial \delta u}{\partial x} \Big _{x_i}$
Width of Slice	$\delta l_i = \lambda_i \delta L$	$\delta l'_i = \lambda'_i \delta L$	$\delta l'_i - \delta l_i = \delta \lambda_i \delta L$

Table 1: Details for how the change in the deformation mapping changes the position, stretch and width of the i^{th} slice. \dagger : In the expression for the stretch of the slice under the mapping φ' , we recognise that $\frac{\partial \delta \varphi}{\partial X} = \frac{\partial \delta u(x)}{\partial X} = \frac{\partial \delta u}{\partial x} \frac{\partial x}{\partial X}$, where in the last equality we've used the chain rule as well as recognising $\frac{\partial x}{\partial X} \Big|_{X_i} = \lambda_i$.

$$\frac{\partial W}{\partial \lambda} \Big|_{T, \lambda_1} = \frac{\partial W}{\partial \lambda} \Big|_{T, \lambda_2} = \frac{W(T, \lambda_2) - W(T, \lambda_1)}{\lambda_2 - \lambda_1}. \quad (20)$$

This allows us to calculate the phase separation stretches λ_1 and λ_2 at each temperature². These stretches then define the coexistence curve, and enclose the shaded coexistence region.

When we abruptly change the temperature of the system, we bring the gel's state out of equilibrium and into different regions of the phase-plane. The gel will then evolve in time, deforming at fixed temperature before reaching new equilibrium. Given the appearance of the phase plane in Fig. 2, we therefore expect the swelling dynamics to be different to the shrinking dynamics. For example, if we abruptly decrease the temperature of a gel, previously at equilibrium with $T_{\text{ini}} = 302K$, to $T_{\text{fin}} = 309K$, our gel will suddenly find itself in the coexistence region, and so we expect to see phase separation. Conversely, if we perform the same temperature change in the opposite direction, the gel will never find itself in the shaded regions and so will never phase separate.

2.5 Small Deformations and Force Balance

Now that we've understood the equilibrium behaviour in our model for thermo-responsive hydrogels at uniform temperature, we move on to consider the thermodynamics of small changes in the deformation that occur when the gel is subjected to an external force. Our variational approach loosely follows the derivation made by Doi [Doi09], with the exception that we consider the chemical potential throughout the gel opposed to the pressure (although, as we shall argue, these are related to one another).

Consider applying an external force f_{ext} to the right-hand-side of a hydrogel submerged in a solvent bath, and let the opposite face of the gel be stuck to an impermeable, stationary wall. The result of the applied force will be to cause a change in the deformation mapping: $\varphi \rightarrow \varphi' = \varphi + \delta \varphi$, such that the material points are displaced from x to new positions, $x' = x + \delta u$ by a small amount, $\delta u(x)$. Assuming the force is applied slowly, so that the gel is constantly in thermal and mechanical equilibrium with its surroundings — i.e. the transformation is quasi-static — what is the change in the free energy of the gel due to the deformation?

Since we're in a uniform temperature field, there's no heating contribution to the free energy - all slices in the gel remain at the same temperature - however the displacement will have caused the stretch in the gel to change slightly. Let's study this change in stretch, in the finite N case, by considering how the i^{th} slice of the gel moves and stretches. Table 1 documents how the position, stretch and width of the i^{th} slice changes due to the change in the deformation mapping.

Now if we sum the changes in free energies over all the slices, we obtain the total change in free energy of the gel:

$$\delta \mathcal{F}_{\text{gel}} = \sum_{i=1}^N F'_i - F_i = A \sum_{i=1}^N \frac{F_i(\lambda_i + \delta \lambda_i) - F_i(\lambda_i)}{v_0} \delta L = A \sum_{i=1}^N \frac{\partial W}{\partial \lambda} \Big|_{X_i} \delta \lambda_i \delta L \quad (21)$$

$$= A \sum_{i=1}^N \frac{\partial W}{\partial \lambda} \Big|_{X_i} \frac{\partial \delta u}{\partial x} \lambda_i \delta L = A \int_0^h \frac{\partial W}{\partial \lambda} \frac{\partial \delta u}{\partial x} dx, \quad (22)$$

where in the second equality we've identified $\varphi(h_0) = h$ as the length of the gel under the deformation φ , and have enforced the left-hand-side boundary condition: $\varphi(0) = 0$. This change in free energy must be accounted for by external work done, to which there are two contributions:

1. the work done by the external force,
2. the work done due to the movement of fluid molecules with non-zero chemical potential.

²When determining the location of the coexistence domain, we actually choose to solve for T and λ_2 at each λ_1 , as this gives more stable results when trying to solve equations (20) numerically.

This first contribution is simple: the force exerted at the right-hand-side boundary causes a displacement $\delta u(x = h)$, so the work done by f_{ext} is:

$$\Gamma_{ext} = f_{ext} \delta u(x = h). \quad (23)$$

The second contribution is more subtle, and so we use the slicing picture to elucidate matters. The change in the deformation may, in general, cause the gel to change its volume - a process that, as discussed in section 2.2, can only come as a result of the absorption or expulsion of fluid. Hence, if the stretch of the i^{th} slice changes by $\delta \lambda_i$, using equation (11), the number of fluid molecules that move into or out of the slice is:

$$\delta n_{f,i} = \frac{v_0}{\Omega_f} \delta \lambda_i. \quad (24)$$

If it takes energy μ_i to add a single fluid molecule to the i^{th} slice - that is, if the chemical potential of the i^{th} slice is μ_i - then the energy to move $\delta n_{f,i}$ molecules will be: $\delta \gamma_\mu = \frac{v_0 \mu_i}{\Omega_f} \delta \lambda_i$. Summing over all the slices, we get the total work done due to fluid movement:

$$\Gamma_\mu = \lim_{N \rightarrow \infty} \sum_{i=1}^N \frac{\mu_i}{\Omega_f} \lambda_i \frac{\partial \delta u}{\partial x} \Big|_{x_i} A \delta L = A \int_0^h \frac{\mu(x)}{\Omega_f} \frac{\partial \delta u}{\partial x} dx. \quad (25)$$

Summing contributions from eqns. (25) and (23) and equating to eqn. (21), we obtain:

$$A \int_0^h \frac{\partial W}{\partial \lambda} \frac{\partial \delta u}{\partial x} dx = A \int_0^h \frac{\mu(x)}{\Omega_f} \frac{\partial \delta u}{\partial x} dx + f_{ext} \delta u(x = h). \quad (26)$$

Taking both integrals over to the left-hand-side and integrating by parts:

$$\left[\left(\frac{\partial W}{\partial \lambda} - \frac{\mu}{\Omega_f} \right) \delta u \right]_{x=0}^{x=h} - \int_0^h \frac{\partial}{\partial x} \left(\frac{\partial W}{\partial \lambda} - \frac{\mu}{\Omega_f} \right) \delta u dx = \frac{f_{ext}}{A} \delta u(x = h). \quad (27)$$

Since the change in the deformation δu was arbitrary, the following relations must hold:

$$\frac{\partial}{\partial x} \left(\sigma - \frac{\mu}{\Omega_f} \right) = 0 \quad \text{in the body,} \quad (28a)$$

$$\sigma(h) - \frac{\mu(h)}{\Omega_f} = \frac{f_{ext}}{A} \quad \text{at the boundary,} \quad (28b)$$

where we have defined the internal stress, $\sigma = \partial W / \partial \lambda$. These equations are simply statements of the requirement for force balance (i.e. mechanical equilibrium) during a quasi-static transformation. An equivalent, more mathematically inclined, derivation is found in (Doi [Doi09]), where variational principles are used, subject to the constraint that the gel volume is conserved when solvent permeation is infinitely slow - an assumption we avoid here, but is central to Doi's argument.

2.6 Setup for Uniform Temperature Changes

Now that we have the appropriate equations for force balance during quasi-static transformations, we take a moment to outline the situation of interest for the remainder of the section. We'd like to study how a 1D TRH in contact with a solvent bath, previously in equilibrium with the ambient temperature, swells or shrinks in response to a change in its temperature. To realise such a system, we take an extended, 3D TRH and attach it to a stationary, impermeable wall. We then encase all but one of the other faces in frictionless, impermeable and stationary walls. The remaining face is then placed in contact with a large solvent bath that supplies fluid molecules at constant pressure p_{bath} , and allowed to exchange fluid with it. An illustration of this set-up is shown in Figure 4.

Figure 4 also shows the uniform temperature distribution throughout the system. Although it isn't shown, we assume that swelling and shrinking behaviour is induced by changing the temperature of a heat bath that makes contact with the system. We also assume the idealised situation where the flow of heat is infinitely fast, an assumption that is justified when compared to the speed at which swelling occurs (Sato Matsuo and Tanaka [ST88]), so that thermal equilibrium between the gel, solvent bath and heat bath is reached instantaneously as the temperature of the heat bath is changed.

In addition, we will consider free-swelling, where the external force applied to the gel's boundary is simply equal to the pressure of the fluid in the bath. This allows us to simplify the boundary condition at the gel's right-hand edge, by considering the energy required to add a single fluid molecule to a fluid at pressure p_{bath} : to open a space of volume Ω_f , we'll need to apply a force $\sim \Omega_f^{2/3} p_{\text{bath}}$ over a distance $\Omega_f^{1/3}$ in each direction, the energy to do which is $3p_{\text{bath}}\Omega_f$. Neglecting the factor of 3 and any energy associated with the

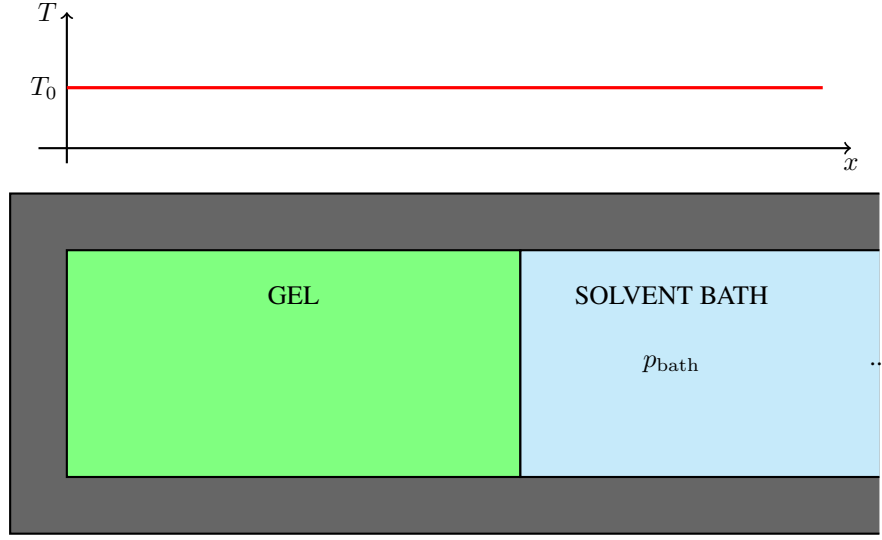


Figure 4: Illustration of a 1D hydrogel in contact with a solvent bath at uniform pressure, p_{bath} , the temperature of which is controlled by an external heat bath (not shown). We assume that the solvent bath is sufficiently large that the gel never reaches the right-hand-side of the solvent bath.

interaction between fluid particles in the bath, the chemical potential of the bath, in terms of its pressure, is: $\mu_{\text{bath}} = p_{\text{bath}}\Omega_f$. Then, by requiring thermal equilibrium between the gel's boundary and the solvent bath, i.e. $\mu(h) = \mu_{\text{bath}}$, equation (28b) is simplified to:

$$\left. \frac{\partial W}{\partial \lambda} \right|_{x=h} = 0. \quad (29)$$

This boundary condition, given the temperature of the system, imposes the value of the stretch at the right-hand-side of the gel.

2.7 Dynamical Equation

We now turn to derive the dynamical equation that governs the time-dependent behaviour of swelling and shrinking hydrogels. Following Bertrand et al. [Ber+16], we treat the hydrogel as a poroelastic medium, and consider the total flux of fluid through the porous polymer network as characterised by Darcy's law:

$$\phi_f(v_f - v_p) = -\frac{k(\phi_f)}{\eta\Omega_f} \frac{\partial \mu}{\partial x}, \quad (30)$$

where $k(\phi_f)$ is the permeability of the solid skeleton, which we take to be constant: $k(\phi_f) = k_0$, η is the dynamic viscosity of the fluid and v_f and v_p represent the velocities of the fluid and polymer network at a given point.

Conservation of fluid and polymer volumes enforce:

$$0 = \frac{\partial \phi_p}{\partial t} + \frac{\partial}{\partial x}(\phi_p v_p), \quad (31a)$$

$$0 = \frac{\partial \phi_f}{\partial t} + \frac{\partial}{\partial x}(\phi_f v_f). \quad (31b)$$

Substituting $\phi_p = 1 - \phi_f$ and adding these equations gives:

$$\frac{\partial}{\partial x} [(1 - \phi_f)v_p + \phi_f v_f] = 0. \quad (32)$$

Then, since the gel is stuck to a stationary, impermeable boundary at $x = 0$, $v_p(x = 0, t) = v_f(x = 0, t) = 0$, the quantity inside the square brackets will be zero everywhere in the gel:

$$(1 - \phi_f)v_p + \phi_f v_f = 0. \quad (33)$$

We then use this to eliminate the polymer velocity from eqn. (30), and find an expression for the fluid flux in terms of the gradient in the chemical potential:

$$\phi_f \left(v_f + \frac{\phi_f v_f}{1 - \phi_f} \right) = -\frac{k_0}{\eta \Omega_f} \frac{\partial \mu}{\partial x} \implies \phi_f v_f = -(1 - \phi_f) \frac{k_0}{\eta \Omega_f} \frac{\partial \mu}{\partial x}, \quad (34)$$

which at the left-hand-boundary is zero:

$$\left. \frac{\partial \mu}{\partial x} \right|_{x=0} = 0. \quad (35)$$

Substituting eqn. (34) into eqn. (31b), we obtain the governing nonlinear partial differential equation for the fluid fraction:

$$\frac{\partial \phi_f}{\partial t} - \frac{\partial}{\partial x} \left(\frac{k_0(1 - \phi_f)}{\eta \Omega_f} \frac{\partial \mu}{\partial x} \right) = 0. \quad (36)$$

It remains to determine the equation for how the length of the gel evolves in time, a result that will prove useful in section 2.9 when we come to numerically solving the model. To derive this, we observe that the total volume of polymer must be conserved (assumption 1):

$$\frac{dV_p}{dt} = \frac{d}{dt} \left(A \int_0^{h(t)} (1 - \phi_f(x, t)) dx \right) = 0. \quad (37)$$

Using the Leibnitz integral rule, we find:

$$\begin{aligned} 0 &= (1 - \phi_f(h(t), t)) \frac{dh}{dt} - \int_0^{h(t)} \frac{\partial \phi_f(x, t)}{\partial t} dx \implies (1 - \phi_f(h(t), t)) \frac{dh}{dt} = \int_0^{h(t)} \frac{\partial}{\partial x} \left(\frac{k_0}{\eta \Omega_f} (1 - \phi_f) \frac{\partial \mu}{\partial x} \right) dx \\ &\implies (1 - \phi_f(h(t), t)) \frac{dh}{dt} = \frac{k_0}{\eta \Omega_f} \left[(1 - \phi_f) \frac{\partial \mu}{\partial x} \right]_0^{h(t)}. \end{aligned}$$

Then, using the boundary condition (35), we find that the rate of change of the gel's length is driven by the gradient in the chemical potential at the RHS boundary.

$$\frac{dh}{dt} = \frac{k_0}{\eta \Omega_f} (1 - \phi_f(h)) \left. \frac{\partial \mu}{\partial x} \right|_{x=h}. \quad (38)$$

2.8 Non-dimensionalisation

Before attempting to solve equations (36), (38) and (28a) subject to boundary conditions (29) and (35), we first introduce the characteristic length, time, stress and energy scales through dimensionless quantities:

$$\tilde{x} = \frac{x}{h_0}, \quad \tilde{t} = \frac{k_0 k_B T_0}{\Omega_{str} \eta h_0^2} t, \quad \tilde{\sigma} = \frac{\Omega_{str}}{k_B T_0} \sigma, \quad \tilde{\mu} = \frac{\Omega_{str}}{k_B T_0 \Omega_f} \mu \quad (39)$$

where h_0 is the dry length of the gel, T_0 is the initial temperature of the gel before the swelling/shrinking begins. These scales are chosen such that the dimensionless equations of motion are as simple as possible:

$$\frac{\partial \phi_f}{\partial \tilde{t}} = \frac{\partial}{\partial \tilde{x}} \left[(1 - \phi_f) \frac{\partial \tilde{\mu}}{\partial \tilde{x}} \right], \quad (40a)$$

$$\frac{\partial \tilde{\mu}}{\partial \tilde{x}} - \frac{\partial \tilde{\sigma}}{\partial \tilde{x}} = 0, \quad (40b)$$

$$\frac{d\tilde{h}}{d\tilde{t}} = (1 - \phi_f(\tilde{h})) \left. \frac{\partial \tilde{\mu}}{\partial \tilde{x}} \right|_{\tilde{x}=\tilde{h}}, \quad (40c)$$

subject to boundary conditions:

$$\left. \frac{\partial \tilde{\mu}}{\partial \tilde{x}} \right|_{\tilde{x}=0} = 0, \quad (41a)$$

$$\tilde{\sigma}(\tilde{h}) = 0. \quad (41b)$$

Now that we have the appropriate equations, for the remainder of the section, we drop all tildes, taking all quantities to be dimensionless.

2.9 Numerical Scheme

For the sake of computational cost, we use the coordinate Z , such that all positions are mapped onto the interval $[0, 1]$. This is achieved by the change of variables: $Z = x/h(t)$, where $h(t)$ is the dimensionless length of the gel at dimensionless time t , and removes the requirement to reshape arrays as the length of the gel evolves. For an arbitrary test function of variables x and t , $\xi(x, t)$, this change of variables alters the partial derivatives:

$$\begin{aligned}\left(\frac{\partial \xi}{\partial t}\right)_x &= \left(\frac{\partial \xi}{\partial t}\right)_Z + \left(\frac{\partial \xi}{\partial Z}\right)_t \left(\frac{\partial Z}{\partial t}\right)_x = \left(\frac{\partial \xi}{\partial t}\right)_Z - \frac{Z}{h} \frac{dh}{dt} \left(\frac{\partial \xi}{\partial Z}\right)_t, \\ \left(\frac{\partial \xi}{\partial x}\right)_t &= \left(\frac{\partial \xi}{\partial Z}\right)_t \left(\frac{\partial Z}{\partial x}\right)_t = \frac{1}{h} \left(\frac{\partial \xi}{\partial Z}\right)_t,\end{aligned}$$

such that the equations of motion read:

$$\frac{\partial \phi_f}{\partial t} = \frac{Z}{h} \frac{dh}{dt} \frac{\partial \phi_f}{\partial Z} + \frac{1}{h^2} \left(\frac{\partial}{\partial Z} \left[k(1 - \phi_f) \frac{\partial \mu}{\partial Z} \right] \right), \quad (43)$$

$$\frac{\partial \mu}{\partial Z} = \frac{\partial \sigma}{\partial Z}, \quad (44)$$

$$\frac{dh}{dt} = (1 - \phi_f(Z = 1)) \frac{1}{h} \frac{\partial \mu}{\partial Z} \Big|_{Z=1}, \quad (45)$$

subject to:

$$\frac{\partial \mu}{\partial Z} \Big|_{Z=0} = 0, \quad (46a)$$

$$\sigma(Z = 1) = 0. \quad (46b)$$

To numerically solve equations (43) - (46b), we use a finite difference scheme to determine the values of the fluid fraction and length at discrete times:

1. Initialise arrays for storing the values of the fluid fraction and temperature at N_z points along interval $[0, 1]$ at each time step, together with the initial gel length.
2. Apply the boundary condition (46b) and set the value of the fluid fraction at the boundary.
3. Calculate the stress, σ at the given time-step.
4. Calculate the gradient in the chemical potential through the gel using eqn. (44).
5. Impose the no flux boundary condition at the gel's left-hand-side (eqn. (41a)).
6. Calculate the rate of change in the gel's length using eqn. (45).
7. Calculate the rate at which ϕ_f changes using eqn. (40a).
8. Use forward-Euler integration to calculate the fluid fraction and gel length at the next time step:

$$\phi_f(t + \Delta t) = \phi_f(t) + \frac{\partial \phi_f}{\partial t} \Delta t, \quad h(t + \Delta t) = h(t) + \dot{h}(t) \Delta t. \quad (47)$$

9. Repeat steps (2)-(9) for the duration of the simulation run.

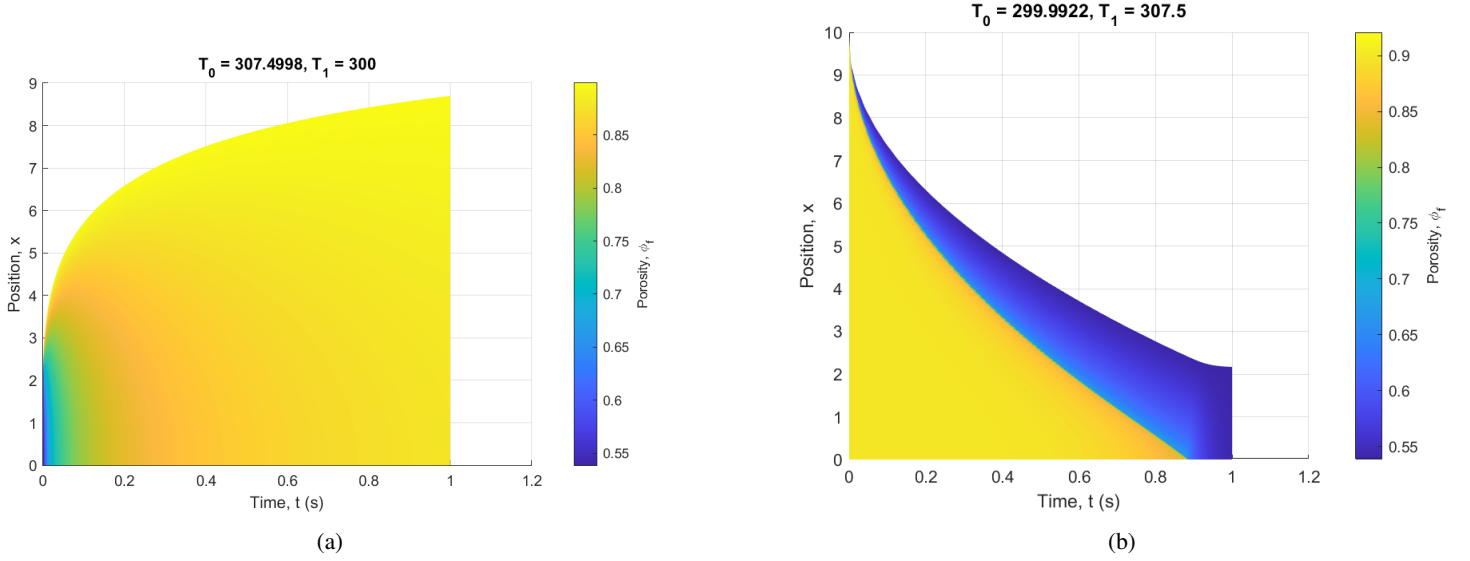


Figure 5: a) Swelling in a 1D thermo-responsive hydrogel after a uniform temperature change from $T_{\text{ini}} = 308 \text{ K}$ to $T_{\text{fin}} = 300 \text{ K}$. b) Shrinking following a uniform temperature change from $T_{\text{ini}} = 308 \text{ K}$ to $T_{\text{fin}} = 300 \text{ K}$. The solver was run using $N_Z = 100$ spatial steps, with a time step $\Delta t = 10^{-6}$. Results were recorded every $t = 10^{-3}$.

2.10 Uniform Temperature Shrinking and Swelling

We briefly present results for large degree shrinking and swelling after a uniform temperature change. In the case of swelling, the temperature is abruptly changed from $T_{\text{ini}} = 308 \text{ K}$ to $T_{\text{fin}} = 300 \text{ K}$, and in the case of swelling, the order of the temperatures is reversed. In figure 5, we show a heatmap displaying how the fluid fraction as a function of position in the gel evolves in time during these processes.

We note the stark difference in the dynamics of swelling and shrinking. In the case of swelling, the gel's right hand edge quickly absorbs fluid, and the gel swells rapidly. As time passes and the gradient in the porosity equilibrates, this rate decreases. After one dimensionless time unit, the gel is still travelling towards equilibrium: the rate of change in the gel's length is still appreciable.

Shrinking, by contrast, is a much faster process: the gel reaches new equilibrium in less than 1 dimensionless time unit. In addition, we observe significant phase-separation as predicted in section 2.4. This starts at the gel's edge in contact with the fluid bath, where a sharp interface separating two coexisting phases progresses towards the left-hand boundary.

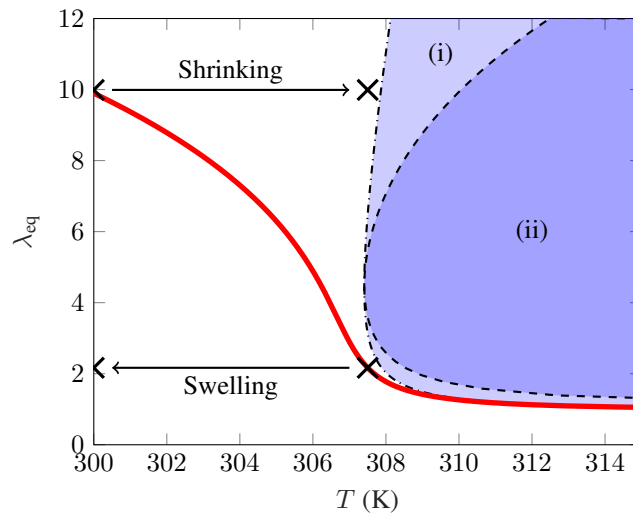


Figure 6: Jumps in phase-space as the temperature of the gel is changed. In the case of shrinking, the gel is initially very close to the coexistence region. As such, during shrinking, it enters the coexistence region and phase separates. Swelling features no phase separation because the gel is initially, and remains, far away from the coexistence and spinodal regions.

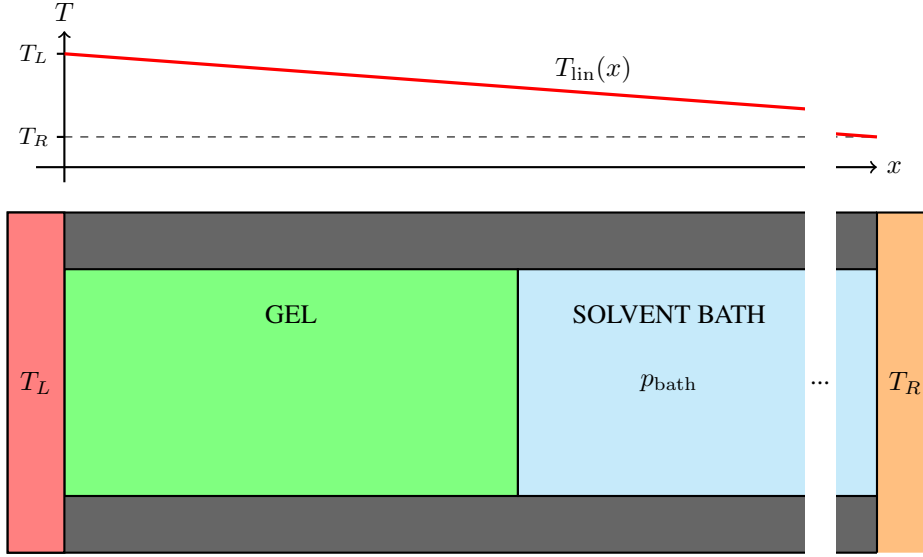


Figure 7: Setup for studying the behaviour of a 1D TRH in a stationary temperature distribution with non-zero temperature gradient, achieved by controlling the temperatures of two heat baths at either end of the system.

3 Dynamics in General Temperature Distributions

Having studied and solved the equations of motion for the thermo-responsive hydrogel system at uniform temperature, we now present the theory for the dynamics of TRHs in general, stationary, temperature distributions. Many of the arguments outlined in the previous section remain the same, with the important exception that the local free energy density now depends on position, not only through the local stretch, $\lambda(x)$, but also through the local temperature it experiences, $T(x)$.

We adjust our setup so that the temperature of the system may be varied by adjusting the temperature of *two* heat baths in contact with the gel and solvent bath at each end. The temperatures of the left and right heat baths are T_L and T_R respectively. An illustration of the set-up is shown in Figure 7.

We consider the scenario where both heat baths are initially at the same temperature, $T_L(t < 0) = T_R(t < 0)$, and where the gel and solvent between them are in thermal and mechanical equilibrium with their surroundings. Then, at $t = 0$, we'll abruptly change the temperature of one of the baths. Assuming infinite thermal diffusivity, the temperature in the gel-solvent container reaches steady-state instantaneously, given by the linear relation:

$$T_{\text{lin}}(x) = \frac{T_R - T_L}{d}x + T_L = \Delta T x + T_L, \quad (48)$$

where d is the spatial separation between the heat baths. Now as the gel evolves, the local temperature in each of its slices will change as they are displaced through the temperature distribution. As such, we expect our force balance to include some kind of thermal stress, and indeed, we find this to be the case.

Before deriving this force balance, we first define what we mean by the 'temperature of a slice'. The concept of an extended, discrete object, having a specific temperature in a continuously varying temperature field $T(x)$ is uncomfortable; an unfortunate artefact of the slicing picture, although we try to ignore these thoughts by defining the temperature of the i^{th} slice as its average temperature. If the i^{th} slice sits at position x_i in a temperature field $T(x)$ and has width δx_i , we take its temperature to be:

$$T_i = \frac{1}{\delta x_i} \int_{x_i}^{x_i + \delta x_i} T(x) dx \approx \frac{1}{\delta x_i} T(x_i) \delta x_i = T(x_i). \quad (49)$$

We then assure the reader that this provides an adequate method for defining the local temperature of the gel as $N \rightarrow \infty$, and our gel becomes a continuum.

3.1 Small Deformations in General Temperature Distribution

Now consider the 1D TRH sitting in a general, stationary temperature distribution. We emphasise that although we are inspired by the distribution with constant temperature gradient (equation (48)), the following derivation applies for any temperature field that is fixed

in time, $T(x)$. We don't consider the effects of temperature distributions that change in time, although we believe our model could be extended to include such situations.

As in section 2.5, consider applying an external force, f_{ext} to the right-hand boundary of the gel, and displacing the material points from $x \rightarrow x' = x + \delta u(x)$. Accompanied by this displacement is the, already familiar, change in stretch in each of the slices: the i^{th} slice experiences a change in stretch, $\delta\lambda_i = \frac{\partial\delta u}{\partial x}\big|_{x_i} \lambda_i$.

However now, the change in the deformation mapping will also move the slices into new regions at different temperatures. Consider the temperatures of the i^{th} slice a) before the displacement: $T_i = T(x_i)$ and b) after the displacement: $T'_i = T(x'_i) = T(x_i + \delta u(x_i))$. The change in temperature of the slice is therefore

$$\delta T_i = T'_i - T_i = \frac{\partial T}{\partial x}\bigg|_{x_i} \delta u(x_i). \quad (50)$$

As before, the total change in the free energy is the sum of the changes in each slice, except the free energy is now actively a function of T :

$$\delta\mathcal{F}_{\text{gel}} = \sum_{i=1}^N F(T_i + \delta T_i, \lambda_i + \delta\lambda_i) - F(T_i, \lambda_i) = A \sum_{i=1}^N \frac{\partial W}{\partial \lambda} \delta\lambda_i + \frac{\partial W}{\partial T} \delta T_i \delta L \quad (51)$$

$$= A \sum_{i=1}^N \frac{\partial W}{\partial \lambda} \frac{\partial \delta u}{\partial x}\bigg|_{x_i} \lambda_i + \frac{\partial W}{\partial T} \frac{\partial T}{\partial x}\bigg|_{x_i} \delta u(x_i) \delta L. \quad (52)$$

Taking the continuum limit:

$$\delta\mathcal{F}_{\text{gel}} = A \int_0^{h_0} \frac{\partial W}{\partial \lambda} \frac{\partial \delta u}{\partial x} \lambda + \frac{\partial W}{\partial T} \frac{\partial T}{\partial x} \delta u \, dX = A \int_0^h \frac{\partial W}{\partial \lambda} \frac{\partial \delta u}{\partial x} + \frac{1}{\lambda} \frac{\partial W}{\partial T} \frac{\partial T}{\partial x} \delta u \, dx. \quad (53)$$

This change in free energy is balanced by the work done due to the external force (eqn. (23)) and by the work done moving the fluid in the gel (eqn. (25)):

$$A \int_0^h \frac{\partial W}{\partial \lambda} \frac{\partial \delta u}{\partial x} + \frac{1}{\lambda} \frac{\partial W}{\partial T} \frac{\partial T}{\partial x} \delta u \, dx = A \int_0^h \frac{\mu(x)}{\Omega_f} \frac{\partial \delta u}{\partial x} dx + f_{ext} \delta u(x=h). \quad (54)$$

Taking the integrals over to the left-hand-side and integrating by parts, we obtain new force balance equations that include a thermal term. We also specialise to the case of free-swelling, where the external force is provided by fluid pressure, $f_{ext}/A = p_{bath} = \mu_{bath}/\Omega_f$ such that:

$$\frac{\partial}{\partial x} \left(\sigma - \frac{\mu}{\Omega_f} \right) = \Sigma_T \quad \text{in the body,} \quad (55a)$$

$$\sigma(h) = 0 \quad \text{at the boundary,} \quad (55b)$$

where the thermal force density Σ_T has been defined as:

$$\Sigma_T = \frac{1}{\lambda} \frac{\partial W}{\partial T} \frac{\partial T}{\partial x} \quad (56)$$

3.2 Dynamical Equations in General Temperature Distribution

Assuming the dynamic viscosity of the fluid is temperature independent, eqn. (36) remains valid, and so the equations of motion for the 1D TRH in a general, stationary temperature field read as:

$$\frac{\partial \phi_f}{\partial t} = \frac{\partial}{\partial x} \left[(1 - \phi_f) \frac{\partial \mu}{\partial x} \right], \quad (57a)$$

$$\frac{\partial \mu}{\partial x} = \frac{\partial \sigma}{\partial x} - \Sigma_T, \quad (57b)$$

$$\frac{dh}{dt} = (1 - \phi_f(h)) \frac{\partial \mu}{\partial x}\bigg|_{x=h}, \quad (57c)$$

subject to boundary conditions:

$$\left. \frac{\partial \mu}{\partial x} \right|_{x=0} = 0, \quad (58a)$$

$$\sigma(h) = 0. \quad (58b)$$

4 Concluding Remarks

To summarise, we have derived the equations governing the swelling and shrinking dynamics of a hypothetical one-dimensional thermo-responsive hydrogel using a poro-elastic model. We proposed a numerical scheme to solve these equations, and briefly presented results illustrating the differences between shrinking and swelling. We then progressed to considered the temperature as a function of position, uncovering a new force present in gels experiencing a temperature gradient. Although we haven't attempted to solve the resulting dynamical equations, we have taken the first step towards studying the dynamics of thermo-responsive hydrogels in more exotic scenarios where, for example, the temperature field might vary with time.

Before closing, we also note that our model makes certain assumptions about the temperature-independence of certain quantities which may not be appropriate - most notably the chemical potential and dynamic viscosity, both of which *do* have temperature dependence. Whether these dependencies play a significant role in the modelling is yet to be seen.

References

- [Ber+16] Thibault Bertrand et al. “Dynamics of Swelling and Drying in a Spherical Gel”. In: *Phys. Rev. Applied* 6 (6 2016), p. 064010. DOI: 10.1103/PhysRevApplied.6.064010. URL: <https://link.aps.org/doi/10.1103/PhysRevApplied.6.064010>.
- [Dim+19] Michael S Dimitriyev et al. “Swelling thermodynamics and phase transitions of polymer gels”. In: *Nano Futures* 3.4 (2019), p. 042001. DOI: 10.1088/2399-1984/ab45d5. URL: <https://doi.org/10.1088/2399-1984/ab45d5>.
- [Doi09] Masao Doi. “Gel Dynamics”. In: *Journal of the Physical Society of Japan* 78.5 (2009), p. 052001. DOI: 10.1143/JPSJ.78.052001. eprint: <https://doi.org/10.1143/JPSJ.78.052001>. URL: <https://doi.org/10.1143/JPSJ.78.052001>.
- [Flo41] Paul J. Flory. “Thermodynamics of high polymer solutions”. In: *The Journal of chemical physics* 9.8 (1941), pp. 660–661.
- [FR43] Paul J. Flory and John Rehner Jr. “Statistical mechanics of cross-linked polymer networks II. Swelling”. In: *The Journal of chemical physics* 11.11 (1943), pp. 521–526.
- [HMW20] Matthew G. Hennessy, Andreas Münch, and Barbara Wagner. “Phase separation in swelling and deswelling hydrogels with a free boundary”. In: *Phys. Rev. E* 101 (3 2020), p. 032501. DOI: 10.1103/PhysRevE.101.032501. URL: <https://link.aps.org/doi/10.1103/PhysRevE.101.032501>.
- [Hug41] Maurice L. Huggins. “Solutions of long chain compounds”. In: *The Journal of chemical physics* 9.5 (1941), pp. 440–440.
- [Ila+81] Michal Ilavsky et al. “Phase transition in swollen gels. 6. Effect of aging on the extent of hydrolysis of aqueous polyacrylamide solutions and on the collapse of gels”. In: *Macromolecules* 17.12 (1981), pp. 2868–2874.
- [Li+17] Xue Li et al. “Reversible bidirectional bending of hydrogel-based bilayer actuators”. eng. In: *Journal of materials chemistry. B, Materials for biology and medicine* 5.15 (2017), pp. 284–2812.
- [RC03] Michael Rubinstein and Ralph H. Colby. *Polymer Physics*. Oxford: Oxford University Press, 2003.
- [Sek93] Ken Sekimoto. “Temperature hysteresis and morphology of volume phase transition of gels”. In: *Physical review letters* 70.26 (1993), pp. 4154–4157.
- [Soo+16] Nikhil Sood et al. “Stimuli-responsive hydrogels in drug delivery and tissue engineering”. In: *Drug delivery* 23.3 (2016), pp. 748–770.
- [ST88] Eriko Sato Matsuo and Toyochi Tanaka. “Kinetics of discontinuous volume–phase transition of gels”. In: *The Journal of Chemical Physics* 89.3 (1988), pp. 1695–1703. DOI: 10.1063/1.455115. eprint: <https://doi.org/10.1063/1.455115>. URL: <https://doi.org/10.1063/1.455115>.
- [Tan+80] Toyochi Tanaka et al. “Phase Transitions in Ionic Gels”. In: *Phys. Rev. Lett.* 45 (20 1980), pp. 1636–1639. DOI: 10.1103/PhysRevLett.45.1636. URL: <https://link.aps.org/doi/10.1103/PhysRevLett.45.1636>.

- [Tan+82] Toyochi Tanaka et al. “Collapse of Gels in an Electric Field”. In: *Science* 218.4571 (1982), pp. 467–469. DOI: 10.1126/science.218.4571.467. URL: <https://www.science.org/doi/abs/10.1126/science.218.4571.467>.
- [TD95] Tsutomu Tomari and Masao Doi. “Hysteresis and Incubation in the Dynamics of Volume Transition of Spherical Gels”. In: *Macromolecules* 28.24 (1995), pp. 8334–8343. DOI: 10.1021/ma00128a050. URL: <https://doi.org/10.1021/ma00128a050>.