Transient instabilities in swelling dynamics

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We investigate the swelling dynamics driven by solvent absorption in a hydrogel sphere immersed in a solvent bath, through an accurate computational model and numerical study. We extensively describe the transient process from dry to wet and discuss the onset of surface instabilities through a measure of the lack of smoothness of the outer surface and a morphological pattern of that surface with respect to the two material parameters driving the swelling dynamics.

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I. INTRODUCTION

Hydrogels are soft materials made of cross-linked networks of hydrophilic polymers; when immersed in water, they swell by absorbing the liquid until a new steady balance between elastic and chemical energy has been reached. The swelling–induced deformations may be very large, and that makes the mechanics of hydrogels especially interesting, and it also forces to set the stress–diffusion problem within the context of nonlinear mechanics [1–8].

The mechanics of hydrogels has attracted a lot of attention since decades [9–12]. Stress diffusion modeling gives important explicit formulas describing both the fast response of the hydrogels before diffusion starts, or the asymptotic response after diffusion-driven relaxation [8, 12]. Nevertheless, explicit results describing the transient dynamics are sought to find, while the numerical solutions of the stress diffusion model is challenging; as already noted in [13], transient dynamics received comparatively little attention despite its practical importance [7, 14–16].

Whereas the surface instabilities which may characterise the steady state of hydrogels being constrained in space and undergoing large volume variations have been largely studied [17–19], the same is not true in the case of transient surface instabilities. An especially interesting transient phenomenon observed during the free swelling of hydrogels is the protrusion of surface patterns on the surface. It happens that, at early times, only a thin surface layer is swollen and the geometric mismatch between this layer and the layers underneath may produce a sufficiently large pressures that make the outer surface to buckle. Surface patterns due to instability have been experimentally observed in both flat and non flat bodies [9, 13, 20–22]. On the other side, the theoretical and/or numerical characterization of the process is still lacking, even if a number of accurate studies have been proposed [13, 16].

Here, we study the swelling dynamics driven by solvent absorption in a hydrogel sphere immersed in a solvent bath, by numerical experiments based on an accurate computational model; in particular, we observe and extensively describe the onset of surface instabilities. The numerical experiments give insight into relevant quantities which are difficult or impossible to measure experimentally, as the stress state or the solvent concentration. We also discuss the role of the two material parameters which completely drive the deformative process through a morphological phase diagram which shows, for some

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choices of the two parameters, the morphology of the outer surface of the sphere.

II. THEORETICAL BACKGROUND

Our starting point is the multiphysics model presented
and discussed in [4] and successively refined in [15], where the
buckling dynamics of a solvent–stimulated and
stretched elastomeric sheet are investigated.

II.1. Displacement and solvent concentration

We introduce a dry-reference state $B_d$ of the gel, and
denote with $X_d \in B_d$ a material point and with $t \in T$ an
instant of the time interval $T$. Our multiphysics model
of gel has two state variables: the displacement field
$u_d(X_d, t)$ ($u_d = \text{m}$), which determines the actual po-
sition $x$, at time $t$, of a point $X_d$ as $x = X_d + u_d(X_d, t)$,
and the molar solvent concentration per unit dry volume
$c_d(X_d, t)$ ($c_d = \text{mol/m}^3$). Key of the model is the volu-
metric constraint coupling the two state variables:

$$J_d = \text{det} \mathbf{F}_d = \hat{J}_d(c_d) = 1 + \Omega c_d,$$  \hspace{1cm} (II.1)

where $\mathbf{F}_d = \mathbf{I} + \nabla u_d$ is the deformation gradient and $\Omega$
is the molar volume, that is, the volume per solvent mole
($[\Omega] = \text{m}^3/\text{mol}$). The constraint (II.1) implies that
any change in volume of the gel is accompanied by uptake
or release of solvent. This in turn entails that the ac-
tual volume-element $dv$ of the body is related to its dry
volume-element $dV_d$ through the solvent concentra-
tion $c_d$, by the formula

$$\frac{dv}{dV_d} = J_d = \hat{J}_d(c_d) = 1 + \Omega c_d. \hspace{1cm} (II.2)$$

The constitutive equation for the stress $\mathbf{S}_d$ ($[\mathbf{S}_d] = \text{Pa}$ =
$J/\text{m}^3$) at the dry configuration $B_d$, henceforth termed
dry–reference stress, and for the chemical potential $\mu$
($[\mu] = \text{J/mol}$) are derived from a relaxed version of the
Flory–Rehner thermodynamic model [23, 24]. It is based
on a free energy $\psi$ per unit dry volume which depends on
$\mathbf{F}_d$ through an elastic component $\psi_e$, and on $c_d$ through
a polymer–solvent mixing energy $\psi_m$: $\psi = \psi_e + \psi_m$.
The relaxed free–energy $\psi_r$ includes the volumetric con-
straint:

$$\psi_r(\mathbf{F}_d, c_d, p) = \psi_e(\mathbf{F}_d) + \psi_m(c_d) - p(\hat{J}_d - \hat{J}(c_d)). \hspace{1cm} (II.3)$$

The pressure $p$ represents the reaction to the volumet-
ric constraint, which maintains the volume change $J_d$
due to the displacement equal to the one due to solvent
absorption or release $\hat{J}(c_d)$. Key features of $\psi$ (or $\psi_r$)
are the following: (i) $\psi$ is a density per unit volume of
the dry polymer; (ii) the elastic contribution $\psi_e$ hampers
swelling; (iii) the mixing contribution $\psi_m$ favors swelling.

II.2. Stress and chemical potential

The constitutive equations for the stress $\mathbf{S}_d$ and the
chemical potential $\mu$ ($[\mu] = \text{J/mol}$) come from dissipation
issues and prescribe that

$$\mathbf{S}_d = \dot{\mathbf{S}}_d(\mathbf{F}_d) - p \mathbf{F}_d' \hspace{0.5cm} \text{and} \hspace{0.5cm} \mu = \dot{\mu}(c_d) + p \Omega,$$ \hspace{1cm} (II.4)

with

$$\dot{\mathbf{S}}_d(\mathbf{F}_d) = \frac{\partial \psi_e}{\partial \mathbf{F}_d} \hspace{0.5cm} \text{and} \hspace{0.5cm} \dot{\mu}(c_d) = \frac{\partial \psi_m}{\partial c_d}, \hspace{1cm} (II.5)$$

where $\mathbf{F}^* = (\text{det} \mathbf{F}) \mathbf{F}^{-T}$. Typically, the Flory–Rehner
thermodynamic model prescribes a neo-Hookean elastic
energy $\psi_e$ and a polymer–solvent mixing energy $\psi_m$:

$$\psi_e(\mathbf{F}_d) = \frac{G}{2} (\mathbf{F}_d - 1)^2 - 3, \hspace{0.5cm} \psi_m(c_d) = \frac{\mathcal{R} T}{\Omega} h(c_d), \hspace{1cm} (II.6)$$

with

$$h(c_d) = \Omega c_d \log \frac{\Omega c_d}{1 + \Omega c_d} + \chi \frac{\Omega c_d}{1 + \Omega c_d}, \hspace{0.5cm} [h] = 1.$$ \hspace{1cm} (II.7)

$G$ being the shear modulus of the dry polymer, $\mathcal{R}$ the
universal gas constant, $T$ the temperature, and $\chi$ the
Flory parameter. Their physical units are $[G] = \text{J/m}^3$,
$[\mathcal{R}] = \text{J/(K mol)}$, $[T] = \text{K}$, while $\chi$, called dis-affinity,
is non dimensional and possibly temperature-dependent;
its value is specific of each solvent-polymer pair: high $\chi$
favours de-swelling, low $\chi$ drives swelling. It is im-
portant to note that $G$ and $\mathcal{R} T / \Omega$ share the same physical
dimensions: they measure the volumetric density of the
elastic and the mixing energy, respectively. The ratio $\varepsilon_m$
between elastic and chemical energy has an important role
in swelling dynamics:

$$\varepsilon_m = \frac{G \Omega}{\mathcal{R} T}. \hspace{1cm} (II.8)$$

From (II.5) and (II.6) we obtain the constitutive equa-
tions for the dry-reference stress $\mathbf{S}_d(\mathbf{F}_d)$ and for chemical
potential $\dot{\mu}(c_d)$; this latter can be rewritten in terms of
$J_d$ by exploiting the volumetric constraint (II.1):

$$\dot{\mathbf{S}}_d(\mathbf{F}_d) = G \mathbf{F}_d, \hspace{1cm} \dot{\mu}(c_d) = \mathcal{R} T \left( \log \frac{J_d - 1}{J_d} + \frac{1}{J_d} + \frac{\chi}{J_d^2} \right). \hspace{1cm} (II.9)$$

The actual stress (Cauchy) $\mathbf{T}$ is then given by the con-
stitutive term $\mathbf{T}(\mathbf{F}_d)$ minus the pressure term

$$\mathbf{T} = J_d^{-1} \mathbf{S}_d \mathbf{F}_d' = \mathbf{T}(\mathbf{F}_d) - p \mathbf{I}, \hspace{1cm} (II.10)$$

with $\mathbf{T}(\mathbf{F}_d) = G / J_d \mathbf{B}$, and $\mathbf{B} = \mathbf{F}_d \mathbf{F}_d'$. 

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{Figure1.png}
\caption{The volume change of volume elements, described by the Jacobian $J_d$, may be interpreted as adding the elementary volume of solvent $\Omega c_d dV_d$ to the dry volume-element $dV_d$.}
\end{figure}
II.3. Solvent flux

A key element in the transient swelling is the solvent flux; here, we assume the following prescription for the reference solvent flux \( \mathbf{h}_d \)

\[
\mathbf{h}_d = \mathbf{h}_d(F_d, c_d, p) = -\mathbf{M}(F_d, c_d)\nabla(\bar{\mu}(c_d) + p\Omega)
\]

(II.11)

which is consistent with the dissipation principle, provided that the mobility tensor \( \mathbf{M}(F_d, c_d) \) is positive definite; \( |\mathbf{M}| = \text{mol}^2/(\text{s m J}) \). Among the many admissible representations for the mobility, here we assume \( \mathbf{M} \) to be isotropic, and diffusion always to remain isotropic during any process (see Ref. [4] for a full discussion on the different isotropic representations for \( \mathbf{M} \)), and linearly dependent on \( c_d \): We have:

\[
\mathbf{M}(F_d, c_d) = \frac{D}{RT} c_d C_d^{-1}, \quad C_d = F_d^T F_d,
\]

(II.12)

with \( D \) \((D) = \text{mol}^2/\text{s}) \) the diffusivity. Using \( \mathbf{m} \) to denote the outward unit normal, \( q = -\mathbf{h}_d \cdot \mathbf{m} > 0 \) is a positive boundary source, that is, an inward flux.

II.4. The Initial-Boundary Value problem

The model is based on a system of bulk equations, describing the balance of forces and the balance of solvent concentration, coupled through the volumetric constraint (II.1), and the constitutive equations (II.4): on \( \mathcal{B}_d \times \mathcal{T} \)

\[
0 = \text{div} \mathbf{S}_d \quad \text{and} \quad \dot{c}_d = -\text{div} \mathbf{h}_d,
\]

(II.13)

with a dot denoting the time derivative and \( \text{div} \) the divergence operator. Equations (II.13) must be complemented with mechanical boundary conditions on the traction \( \mathbf{t} \) and/or displacement \( \mathbf{u}_d \):

\[
\mathbf{S}_d \mathbf{m} = \mathbf{t}, \quad \partial_t \mathcal{B}_d \times \mathcal{T},
\]

(II.14)

\[
\mathbf{u}_d = \mathbf{u}_d, \quad \partial_u \mathcal{B}_d \times \mathcal{T};
\]

and with chemical boundary conditions on solvent source \( q_s \) and/or concentration \( c_s \):

\[
-\mathbf{h}_d \cdot \mathbf{m} = q_s, \quad \partial_u \mathcal{B}_d \times \mathcal{T},
\]

\[
c_d = c_s, \quad \partial_u \mathcal{B}_d \times \mathcal{T}.
\]

(II.15)

Notation \( \partial_u \mathcal{B}_d \) with \( s = t, u, q \) or \( c \) in the above equations denotes the portion of the boundary of \( \mathcal{B}_d \) where traction \( \mathbf{t} \), displacement \( \mathbf{u}_d \), flux \( q_s \), and concentration \( c_s \) are prescribed, respectively. Finally, the model is completed by the initial conditions for the state variables \( \mathbf{u}_d \) and \( c_d \):

\[
\mathbf{u}_d = \mathbf{u}_{d,0}, \quad c_d = c_{d,0}, \quad \text{on} \mathcal{B}_d \times \{0\}
\]

(II.16)

III. SWELLING EQUILIBRIUM OF A GEL SPHERE

We now consider a spherical gel and reformulate the initial-boundary problem assuming radial symmetry, that is, assuming \( \mathbf{u}_d = u_R(R, t) \mathbf{m} \) with \( R \) the radial coordinate and \( \mathbf{m} \) the unit radial vector, and \( c_d = c_d(R, t) \). Under these assumptions, the balance equations (II.13) rewrites as

\[
\begin{align*}
S_R' + \frac{2}{R}(S_R - S_\theta) &= 0, \quad c_d = -(h'_R + \frac{2h_R}{R}),
\end{align*}
\]

(III.17)

with \( S_R \) and \( S_\theta \) the radial and hoop components of the dry–reference stress \( \mathbf{S}_d \), \( h_R \) the unique component of the flux vector \( \mathbf{h}_d(R, t) = h(R, t) \mathbf{m} \), and a prime denoting derivation with respect to the radial coordinate. On the boundary, we have zero radial stress \( S_R = 0 \), and a concentration \( c_s \) determined by the external chemical potential \( \mu_{\text{ext}} \), that is, equation \( \bar{\mu}(c_s) + p\Omega = \mu_{\text{ext}} \) holds. The constitutive equations determine the stress components

\[
S_R = G\lambda_R - \lambda_3^2 p, \quad S_\theta = G\lambda_\theta - \lambda_\theta \lambda_R p,
\]

(III.18)

as well as the flux field

\[
h(R, t) = -\frac{D}{RT} c_d(R, t)\lambda^{-2}_R(R, t)p'(R, t),
\]

(III.19)

where \( \lambda_R = r' \) and \( \lambda_\theta = r/\theta \) are the radial and hoop stretches and \( r(R, t) = R + u_R(R, t) \) the actual radius. With this, equations (III.17) can be written as

\[
\dot{c}_d = \frac{1}{R^2}\left[\frac{D}{RT} \frac{c_d}{\lambda^2_R} R^2 \left(\frac{\partial h}{\partial c_d} c'_d + \Omega p'\right)\right],
\]

(III.20)

Together with the incompressibility condition, which can be integrated and inverted to get

\[
r(R, t) = \left[ R^3 + 3 \Omega \int_0^R \phi c_d(\phi, t) d\phi \right]^{1/3}
\]

(III.21)

equations (III.20) can be numerically integrated to describe swelling evolution under spherically symmetric conditions. The steady fully-swollen state at \( \mu_{\text{ext}} = 0 \) is characterized by an uniform concentration \( c_\infty \) and an uniform swelling ratio \( \lambda_R = \lambda_\theta = \lambda_\infty \), with \( \lambda_\infty = \frac{\lambda_{\text{ext}}}{\Omega} \).
(1 + \Omega c_\infty)^{1/3}. Such a state can be determined by solving the evolutive problem (III.20).

Alternatively, both \lambda_\infty and c_\infty can be determined directly as solution of the steady problem: S_d = 0 and \mu = 0. From (II.4), (II.5), and assuming that \mathbf{F} = \lambda_\infty \mathbf{I}, we have
\[
\log(1 - \frac{1}{\lambda_\infty^3}) + \frac{1}{\lambda_\infty^3} + \frac{\chi}{\lambda_\infty^5} + \frac{\epsilon_m}{\lambda_\infty^2} = 0.
\] (III.22)

Typically we have \lambda_\infty >> 1 (that is, 1/\lambda_\infty << 1), and equation (III.22) can be approximated as
\[
\epsilon_m \lambda_\infty^8 + (\chi - 1/2) \lambda_\infty^3 - \frac{1}{3} = 0,
\] (III.23)

thus assuming the form of a singular perturbation. The leading order, as already shown in [25–27], yields
\[
\lambda_\infty \approx \left(\frac{1 - 2\chi}{2\epsilon_m}\right)^{1/5}.
\] (III.24)

It is worth noting that a scaling analysis based on: i) the length scale A, with A the radius of the sphere at dry-reference; ii) the characteristic time scale t_c = A^2/D; iii) the shear modulus G, shows that both the swimming dynamics and the steady solution are scale–free, and only depend on the material parameters \chi and \epsilon_m.

However, as experiments showed [13], swimming dynamics is not spherical symmetric at early and intermediate times, when wrinkles appear on the surface (see figure 2). Hence, we propose a refined computational analysis based on the theoretical model shown in Section II.3 which allows us to highlight the pattern characteristics as well as the dependence on the material parameters.

IV. FINITE ELEMENTS ANALYSIS OF SWELLING DYNAMICS

The Finite Elements Model (FEM) solves balance equations (II.13) and the volumetric constraint (II.1) in a weak form as
\[
0 = \int_{B_d} \left(- (S_d (F_d) - p F_d') \cdot \nabla \hat{u}_d, \right.
\]

\[
0 = \int_{B_d} \left[ - \tilde{c}_d \cdot \hat{c}_d + h_d \cdot \nabla \tilde{c}_d \right],
\] (IV.25)

\[
0 = \int_{B_d} \left[ J_d - (1 + c_d \Omega) \right] \cdot \hat{p},
\]

where the tilde indicates a test field. We note that the unknown pressure p is considered as an additional state variable, having the role of a Lagrange multiplier.

Boundary conditions (II.14) are quite easy to handle, as we set t = 0, and assign a displacement \hat{u}_d that eliminates any rigid motion without generating reaction forces.

Tackling the chemical boundary conditions (II.15) is more tricky, as it is not possible to control the surface flux source q_s, nor the surface concentration c_s. Actually, what is done in real experiments, and what we aim at replicating in our numerical model, is the control of the chemical potential \mu_{ext} of the bath on \partial B_d \times T.

In the present model, it is equation (II.4), evaluated at the boundary, that relates \epsilon_s to \mu_{ext}; this is a highly non-linear equation which cannot be solved for \epsilon_s; moreover, as we control the state variable \epsilon_s, the surface flux source q_s must be considered as a reaction, which is unknown a priori, and whose evaluation a posteriori yields poor approximations.

Those two issues are solved by posing in weak form both relation (II.4), and the constraint (II.15).

\[
0 = \int_{\partial B_d} \left[ \mu(c_s) + p \Omega - \mu_{ext} \right] \cdot \hat{c}_s,
\] (IV.26)

\[
0 = \int_{\partial B_d} \left[ (c_d - c_s) \hat{q}_s + q_s (\hat{c}_d - \hat{c}_s) \right].
\] (IV.27)

It is important to note that we use the same technique as before, that is, we enforce the constraint c_d = c_s by considering q_s as an additional state variable, having the role of a Lagrange multiplier; as well known, weak constraints provide a far better numerical evaluation of the boundary source q_s.

The complete problem can be reformulated as follows: find \mathbf{u}_d, c_d, p, c_s, and q_s such that, for any test functions \hat{u}_d, \hat{c}_d, \hat{p}, \hat{c}_s, and \hat{q}_s, equations (IV.25)–(IV.27) hold; the three fields \mathbf{u}_d, c_d, p are defined in \mathcal{B}_d \times \mathcal{T}, while the two fields c_s and q_s are defined on \partial B_d \times \mathcal{T}.

IV.1. General analysis of dynamics

We consider a sphere that is initially at equilibrium in nearly dry conditions, with \lambda_\infty \approx 1.02, corresponding to c_{do} = 1006 mol/m^3 and \mu_{ext} \approx -6500 J/mol [28].

\[
J_d
\]

Figure 3. Evolution of the surface patterns from the initial state, \tau = 0, to the final steady state, \tau = 1. Colormap shows the values of J_d.

When the sphere is immersed in water at \mu_{ext} = 0, it swells until a new spherical steady state is reached, having radius \alpha > A. The steady fully-swollen state is characterized by a uniform concentration field c_\infty and a swelling ratio \lambda_\infty. With our choice of parameters, \lambda_\infty \approx 3.8 (see Table I). Let \tau = t/(\alpha t_c) be a non dimensional time; we assign a time evolution law for the external
chemical potential such that \( \mu_{\text{ext}} \) smoothly change from the initial value \( \mu_{\text{ext}}^0 = -6500 \) J/mol, to the final one \( \mu_{\text{ext}}^\infty = 0 \) J/mol, in a time interval \( \tau_c << t_c \). In particular, we define:

\[
\mu_{\text{ext}}(\tau) = \mu_{\text{ext}}^0 + (\mu_{\text{ext}}^\infty - \mu_{\text{ext}}^0)(1 - \exp(-\tau/\tau_c)). \quad (\text{IV.28})
\]

At \( \tau = 0 \) the sphere is in almost dry conditions; at early times, \( \tau << 1 \), the swelling dynamics produces surface patterns which alters the spherical symmetry; such patterns disappear when the swelling evolves, and before approaching the steady state, the gel completely recovers its smooth spherical shape (see figure 3). Surface patterns are due to surface instabilities, which have been largely studied in growing soft materials [29–32], even if, at the best of our knowledge, a 3D computational analysis based on a fully nonlinear multi-physics model of the swelling is still lacking. Our model allows to highlight the characteristics of swelling dynamics when surface instabilities appear, evolve, and disappear. At first, we define the hoop component \( \sigma_\theta \) of the actual stress (Cauchy), made of the constitutive part \( \hat{\sigma}_\theta \), minus the indeterminate pressure \( p \):

\[
\sigma_\theta = \hat{\sigma}_\theta - p, \quad \text{with} \quad \hat{\sigma}_\theta = \hat{T}(\mathbf{F}_d) \mathbf{e}_\theta \cdot \mathbf{e}_\theta, \quad (\text{IV.29})
\]

where \( \mathbf{e}_\theta \) is a the unit vector orthogonal to \( \mathbf{m} \).

According to the physical expectations and experimental observations [13], at early times we observe a rapid swelling confined in a thin volume near the outer boundary, which is adjacent to an almost un-swollen core.

Figure 4 shows the contour plot of \( \Omega_{cd} \) versus \( R/A \) and \( \tau \); at early times, in the range \( \tau \in (1e^{-5}, 1e^{-2}) \) it appears a thin boundary layer (red colored) where \( \Omega_{cd} \) is quite higher with respect the values it attains in the un-swollen core (blue colored). Analogously, figure 5 shows that, within the same time interval, the boundary layer is under negative hoop stress (compressive stress), meanwhile in the larger zone beneath the boundary layer, the hoop stress is positive (tensile stress).

With the contour plot of \( \sigma_\theta/G \) we can track the time evolution of the boundary between the compressive and the tensile regions, and verify the relationship between zones having high solvent gradient and compressive hoop stress.

| Parameter          | Symbol and value |
|--------------------|------------------|
| Shear modulus      | \( G = 50 \) kPa |
| Dis-affinity       | \( \chi = 0.4 \) |
| Molar volume       | \( \Omega = 1.8 \times 10^{-5} \) m\(^3\)/mol |
| Time scaling       | \( \alpha = 3 \times 10^4 \) |

Figure 2: Results of head-clamped fish (small displacements) and free fish (large displacements) with frequency and wavelength for free fish. (C) Tail amplitude VS frequency and wavelength for head-clamped fish. (D) Tail amplitude VS frequency and wavelength for free fish.

Figure 4: Contour plot of the volume change \( \Omega_{cd} \) versus the dimensionless radius \( R/A \), and time \( \tau \) (in log scale); at early times, in the range \( \tau \in (1e^{-5}, 1e^{-2}) \) it appears a thin layer at the outer surface, that is, solvent remains confined in a small volume. Only for \( \tau > 1e^{-2} \) solvent enters deep in the gel, and becomes uniformly distributed for \( \tau \approx 1 \).

Figure 5: Contour plot of the dimensionless hoop stress \( \sigma_\theta/G \) versus the dimensionless radius \( R/A \), and time \( \tau \) (in log scale); in the same time range \( \tau \in (1e^{-5}, 1e^{-2}) \), a thin region under compression appears near the outer surface. Moreover, pressure rapidly changes from negative to positive when moving towards the center of the sphere. Both features evidenced in the figures. 4 and 5 are the signature of wrinkling.
and known as the effective stress in porous-mechanics; the second one \( p/G \) represents the mechanical contribution to the dimensionless chemical potential as equation (II.4) shows.

Figures 7 and 8 show that \( p/G \) has a key role in determining the compressed region: while the effective stress \( \hat{\sigma}_\theta/G \) is monotone decreasing both at the boundary and inside the sphere, the pressure behaves very differently. On the boundary of the sphere, \( p/G \) increases very fast from the initial value, and remains always greater than \( \hat{\sigma}_\theta/G \) (top panel); conversely, at the center \( p/G \) decreases very fast from the initial values, and remains always smaller than \( \hat{\sigma}_\theta/G \) (bottom panel). The two summands of the stress attain the same value at \( \tau = 1 \), which correspond to a steady, stress-free state.

So, the stress state of the sphere is similar to the one we find in a circumferentially growing thick shell due to the residual stresses triggered by growth: tensile in the inner layer and compressive in the outer one [29]. Likewise, both hoop and radial strains \( \lambda_\theta \) and \( \lambda_R \) are always larger than 1 on the outer surface, and drive the swelling-induced hoop and radial growth of the sphere (see figure 6). We can evaluate the volume \( V_s \) of solvent crossing the boundary during the dimensionless time interval \((0,1)\), as well as its time rate \( V_s \), that is, the volume of solvent crossing the boundary per unit of dimensionless time:

\[
V_s = \int_0^1 \dot{V}_s \, t_c \, d\tau \quad \text{and} \quad \dot{V}_s = \Omega \int q_s \, dA_d, \quad (IV.30)
\]

being \( \Omega q_s \) (\( [\Omega q_s] = \text{m}^3/(\text{s} \cdot \text{m}^2) \)) the volume of solvent crossing the boundary per unit time and unit area. Figure 10 shows that the rate \( \dot{V}_s \) is especially high at early times. Finally, we show the evolution of the dimensionless radius \( a_i/R \) (\( i = 1, 2, 3 \)), with \( a_i \) the radius of the contour level of the solvent uptake \( \Omega c_{di} \); with set \( \Omega c_{d1} = 1, \ \Omega c_{d2} = 5, \text{ and } \Omega c_{d3} = 10 \). Interestingly, as we expected and in contrast with the measurements made via a shadowgraph technique and presented in [13](Appendix 1), the dimensionless radius \( a_i/A \) always decreases for any choices of the threshold value \( \Omega c_{di} \).
IV.2. Surface instabilities

To quantify the bumpiness of the spherical surface we introduce two different measures, one based on the surface area, the other on the surface gradient of the displacement. The actual, non dimensional area $S_{wr}$ of the spherical gel, be it wrinkled or not, is given by

$$S_{wr} = \frac{1}{4\pi A^2} \int_{\partial B_d} |F^d_\delta m| dA_d , \quad F^\star_\delta = J_\delta F_d^{-T} , \quad (IV.31)$$

being $|F^d_\delta m|$ the ratio between the swollen area element and the corresponding area element $dA_d$ of the dry surface. Then, we introduce the non dimensional area $S_{sm}$ of the mean sphere

$$S_{sm} = \frac{4\pi \bar{r}^2}{4\pi A^2} ; \quad \bar{r} = \frac{1}{4\pi A^2} \int_{\partial B_d} r(t) dA_d , \quad (IV.32)$$

being $\bar{r}$ the average radius of the actual outer surface. The evolution of the difference $\Delta S = S_{wr} - S_{sm}$ shows a peak during the critical time interval, when surface instabilities attain their maximum value, as figure 11 shows (left panel), together with a qualitative view of surface profile (right panel). The other measure of the bumpiness of the external surface is based on the surface gradient

$$\nabla u_R$$

of the radial displacement $u_R$. Given the surface projector $P_s = (I - m \otimes m)$, we define

$$\nabla_s u_R = P_s \nabla u_r , \quad \nabla_s u_R = \frac{1}{4\pi A^2} \int_{\partial B_d} \|\nabla_s u_r\| dA_d , \quad (IV.33)$$

where $\|\nabla_s u_r\| = (\nabla_s u_r \cdot \nabla_s u_r)^{1/2}$ is the norm of $\nabla_s u_r$. The mean surface gradient $\nabla_s u_R$ is not monotone in time and has its maximum $(\nabla_s u_R)_{max}$ at $t_p$, as figure 12 shows.

To assess the influence of the two material parameters $G$ and $\chi$ on the bumpiness of the sphere, we ran a series of analyses with $G = (0.5e5 Pa, 1e5 Pa, 5e5 Pa)$, and $\chi = (0.4, 0.5, 0.6)$. We present the result of our analyses through a morphological phase diagram showing the patterns on the outer surface of the sphere, the value of $(\nabla_s u_R)_{max}$ and of $t_p$ for each choice of the two parameters. As expected, the minimum value of $(\nabla_s u_R)_{max}$ corresponding to an almost smooth outer surface is attained for the highest values of $G$ and $\chi$, both determining a reduced swelling due to the high elastic stiffness $G$ of the polymeric network and to a larger dis–affinity $\chi$ between solvent and polymer.

V. CONCLUSIONS

We presented an extensive computational study of the swelling dynamics driven by solvent absorption in a hydrogel sphere immersed in a solvent bath, based on a fully three–dimensional nonlinear stress–diffusion model. In particular, we observed and described the onset of surface instabilities, introducing appropriate measures of the surface bumpiness. To catch surface patterns due to the high and fast swelling in the the thin surface outer layer, we formulated the boundary conditions on solvent flux and concentration in a form of weak constraints, so providing a better numerical evaluation of the boundary flux which is the determinant of the surface instabilities.
The analysis gives insight into relevant quantities which are difficult or impossible to measure experimentally, as the stress state or the solvent concentration, also showing key differences with other characteristics wrinkling patterns observed during swelling–induced growth.

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Figure 13. Morphological phase diagrams of emerging surface patterns from numerical simulations. The different surface morphologies are displayed for varying values of the material parameters $G$ and $\chi$. The value $|\nabla^s u_r|_m$ as well as the time $\tau_p$ when that value is attained are shown for each pair of material parameters.