



# Mechanics and physics of the light-driven response of hydrogels

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## ABSTRACT

Hydrogels are versatile and environmentally sensitive materials having appealing and tunable physical-chemical-mechanical properties, similar to those encountered in natural living tissues, which enable their use in a wide range of applications, especially in the biomedical field. In the present study, we investigate the temperature-driven responsiveness of one class of elastomeric gels, namely poly-N-isopropylacrylamide (pNIPAm), that allows for temperature-controlled swelling. In particular, we consider the mechanical behavior of temperature-sensitive hydrogels in which the temperature variation is the result of light-thermal conversion enabled by nanoparticles embedded in the material. Relying on a theoretical multi-physics-based model describing light diffusion, heat generation and transfer, fluid absorption, and mechanics, the morphing response of hydrogel elements is investigated. The complex interplay between fluid uptake (swelling) and mechanical deformation taking place at different temperatures is investigated. In particular, the light-driven swelling response of hydrogel under a time-dependent light stimulus is studied. It is shown that the self-cooling of the material influences the material responsiveness. Accordingly, we demonstrate the interplay between the generated and the dispersed heat, which is a key aspect for an efficient design of tunable devices and materials.

## 1. Introduction

Gels are made of an elastomeric network keen to absorb low molecular weight solvent; when such a solvent is water, they are termed hydrogels. The fluid that diffuses into gels per unit initial polymer volume, whose amount depends on the solid-fluid interaction, can be significant and result in a large volume increase [1–3]. Hydrogels are characterized by many attractive properties, such as high-water content, softness, high deformability, biocompatibility, temperature responsiveness, and permeability to gases, which make them ideal candidates for various bio-related and other applications.

If properly controlled and guided to occur in well-defined regions of a gel-based structure, the large volume increase (swelling) enables obtaining deformations at will. The above-described deformation response is of particular interest when the amount fluid uptake by the network can be controlled through environmental stimuli such as temperature, pH, light radiation, presence of particular ions or molecules, enzymes, electrical and/or magnetic field, etc. [4–6]. When the material is able to modify its mechanical state according to the external stimuli, it can be regarded as a responsive, active or smart material [7]. Owing to the biocompatibility and the consistency of hydrogels, which is similar

to that of biological tissues, and their biocompatibility, these materials are commonly used in biologically related applications, especially when their responsiveness is triggered by stimuli that can be generated in living environments.

The physics and mechanics of hydrogels and the related governing equations are well established in the literature [8,9] and have been used to simulate a variety of hydrogel-based elements [10,11].

In the present study, we consider the responsiveness of a particular class of hydrogels whose affinity with the fluid is strongly dependent on the temperature. Within this class of gels, Poly(N-isopropylacrylamide) (pNIPAm) hydrogels are quite relevant [12]. In aqueous solution and at low temperature (below a critical value, see below), pNIPAm has a good affinity with water and is thus in the swollen state. On the other hand, at higher temperatures it switches to a collapsed state, characterized by a low affinity with water leading to deswelling with a consequent volume decrease. The swelling-deswelling phenomenon can be interpreted as a phase transition [13], and it has been explained in terms of molecular transformations [14]; the monomer structure of pNIPAm hydrogels is characterized by amide (–CONH–) and propyl (–CH(CH<sub>3</sub>)<sub>2</sub>) moieties which behave as follows: at low temperature, the amide hydrophilic group is hydrated thanks to hydrogen bonds with water (responsible for

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the above mentioned swollen phase), while above a well-defined volume phase transition temperature (VPTT,  $T_{LH}$  in the case of pNIPAM hydrogels) the interactions between the hydrophobic groups increase, leading to a fluid loss and a corresponding polymer network shrinkage (collapsed phase), i.e. to a strong reduction in volume [15] (Fig. 1).

Among various stimuli suitable to induce responsiveness, the thermal one is probably the most important for health-related applications; smart thermoresponsive PEG/Poly(N-isopropylacrylamide, pNIPAm) polymers are quite relevant in this context thanks to their biocompatibility, biodegradability, and controllable characteristics [16].

The development of responsive materials and structures, especially for applications at small scales such as nano robots, small soft actuators, and micropumps, has known a tremendous effort in the last decades. In particular, materials capable of autonomously responding to environmental stimuli through large mechanical deformations (morphing) are of particular interest [7]. Especially in small scale applications, the possibility to drive actuation in an untethered fashion is quite desirable and has been explored in recent studies [17]. Organizing the material in proper 2D or 3D patterns increases the range of possibilities offered by hydrogel-based devices in obtaining tailored morphing structures [18]; within this context, the advantages of using modern additive manufacturing technologies are quite relevant, as they enable the production of complex architectures and microstructures that are not possible with traditional production techniques [19].

The paper is organized as follows: Sect. 2 presents the main governing equations involved in the swelling phenomenon and the temperature dependence of a particular class of hydrogels is illustrated. Sect. 3 illustrates a micromechanical-based model for polymer networks, while sect. 4 provides some insights into the multi-physics couples problem arising in light driven actuation of temperature-sensitive hydrogels. Some relevant numerical examples are presented in Sect. 5 and, finally, Sect. 6 presents some closing remarks and a discussion on the topic.

## 2. Polymer-fluid interaction in gels

### 2.1. Network-solvent equilibrium

The process of fluid diffusion within a gel network is driven by the osmotic pressure and reaches an equilibrium state when the balance with the forces induced by the deformation of the polymer backbone takes place. It is commonly assumed that the network and the fluid are individually incompressible; thus, the volume increase of the network in its swollen state is equal to the volume of the incoming fluid. Let  $\mathbf{X}(\mathbf{x})$  denote the position of a point in the initial (reference) configuration  $\mathcal{B}_0$  ( $\mathcal{B}$ ) of the body occupying the volume  $V_0(V)$ , while  $\partial\mathcal{B}_0$  ( $\partial\mathcal{B}$ ) is the boundary of the domain with surface area  $A_0$  ( $A$ ), respectively. The deformation of the body is described by the displacement field function  $\omega(\mathbf{X})$  and the deformation gradient tensor is  $\mathbf{F} = \mathbf{1} + \partial\omega(\mathbf{X})/\partial\mathbf{X}$ , where  $\mathbf{1}$  is the second order unit tensor. Upon swelling, the volumetric deformation is given by:  $J = \det \mathbf{F} = 1 + C_s v_s$ , with  $C_s$  the actual solvent concentration referred to the initial configuration and  $v_s$  the molar volume of a fluid molecule; the last relationship enforces the overall volumetric deformation to be equal to the initial volume of the network plus the

diffused fluid (molecular incompressibility). The fluid conservation equation in the current configuration,  $\partial c_s / \partial t + \nabla_{\mathbf{x}} \cdot \mathbf{j} = 0$ , can be written by adopting the Fick's constitutive law  $\mathbf{j} = -\frac{C_s D}{k_B T} \nabla \mu$ , which relates the fluid flux ( $\mathbf{j}$ ) to the chemical potential ( $\mu$ ). Here,  $D$  is the diffusion coefficient,  $T$  is the absolute temperature, and  $k'_B = k_B A_n$  with  $k_B$ ,  $A_n$  the Boltzmann constant and the Avogadro's number, respectively. The concentration  $C_s$  is a function of the chemical potential  $\mu$  and the hydrostatic osmotic pressure  $\pi$  due to the fluid permeating the gel network, which enforces the incompressibility of the gel. Accordingly, we can express the time rate of the concentration as  $\dot{C}_s = \frac{\partial C_s}{\partial t} = \frac{\partial C_s}{\partial \mu} \dot{\mu} + \frac{\partial C_s}{\partial \pi} \dot{\pi}$  [8]. In the deformed configuration the fluid conservation equation reads:

$$J^{-1} \left[ \frac{\partial C_s}{\partial \mu} \dot{\mu} + \frac{\partial C_s}{\partial \pi} \dot{\pi} - \frac{C_s D}{k'_B T} \nabla^2 \mu \right] = 0 \quad (1)$$

where the solvent concentration in the deformed state has been expressed as  $c_s = J^{-1} C_s$ .

The solid-fluid equilibrium can be determined as the stationarity condition of the energy density of the gel:

$$\Psi_{gel} = [\Psi_{net}(\mathbf{F}) + \Psi_{mix}(C_s, T)] + \pi[(1 + v_s C_s) - J] \quad (2)$$

where  $\Psi_{net}$  is the deformational energy of the network,

$$\Psi_{mix} = \frac{k'_B T}{v_s} \left[ (J - 1) \ln \left( \frac{v_s C_s}{J} \right) + v_s C_s \frac{\chi(C_s, T)}{J} \right] \quad (3)$$

is the energy of mixing, and  $\chi$  is the Flory-Huggins (FH) polymer fluid interaction parameter [1].

### 2.2. Temperature-dependent swelling

pNIPAM is one of the most commonly used thermosensitive polymers; its temperature-dependent response comes from its structure, which is made of hydrophilic amide ( $-\text{CONH}-$ ) groups and hydrophobic isopropyl ( $-\text{CH}(\text{CH}_3)_2$ ) side chains. The hydrophilic-hydrophobic transition takes place at a temperature  $\sim 32^\circ\text{C}$ . Since this temperature is comparable to that of the human body, pNIPAm can be exploited in a wide variety of applications in the biomedical field [20].

For temperature-dependent gels, the FH interaction parameter for pNIPAm is often written in the form [21]:

$$\chi_a(C_s, T) = \chi(J, T) = \chi_0(T) + \chi_1(T)/J \quad (4)$$

where  $\chi_0(T, J) = A_0 + B_0 T$ ,  $\chi_1(T) = (A_1 + B_1 T)/J$  and  $A_0, A_1, B_0, B_1$  are model parameters (in our simulations we take  $A_0 = -12.947$ ,  $B_0 = 0.04496 \text{ K}^{-1}$ ,  $A_1 = 17.920$ ,  $B_1 = -0.0569 \text{ K}^{-1}$ , [15]). Another expression that accounts for a temperature-induced transition between low and high interaction parameter values has been proposed in [9]:

$$\chi_b(T) = \frac{\chi_L + \chi_H}{2} + \frac{\chi_H - \chi_L}{2} \tanh \left( \frac{T - T_{LH}}{c} \right) \quad (5)$$

where  $\chi_L, \chi_H$  are the FH parameter values below and above the transition temperature  $T_{LH}$ , respectively, and  $c$  is a fitting parameter.

By using Eq. (4), the emerging energy landscape is illustrated in Fig. 2 where the quantity  $\Psi_{gel} = \Psi_{net} + \Psi_{mix}$  is displayed for a material allowed to swell freely in 1 or in 3 directions according to the applied constraints [21].

It can be noticed that the volume ratio  $J$  at equilibrium is strongly dependent on  $T$ , and so the amount of fluid uptake by the network can be tuned by modifying the temperature.

### 2.3. Photo-thermal heating in a semi-transparent medium

The activation of pNIPAm hydrogels can be controlled by inducing heat through the photo-thermal effect. This is achieved by embedding particles in the hydrogel matrix which generate heat from inside the gel,

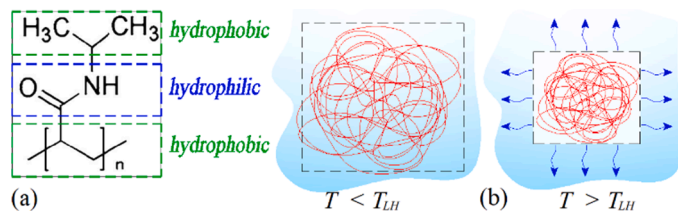


Fig. 1. Schematic of a temperature-sensitive gel displaying swelling or deswelling according to the temperature value.

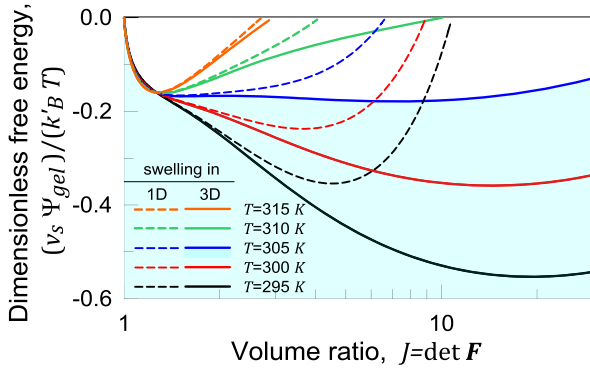


Fig. 2. Free energy of a temperature-sensitive gel vs volume ratio  $J$  for various temperatures. The transition temperature is around  $T = 305$  K.

thereby forcing water molecules out. To quantify the generated heat, one must define a constitutive equation for the intensity of the light field  $I(\mathbf{X}, t)$ ; to this end, we follow the Beer-Lambert light diffusion equation [22]

$$\begin{aligned} I(\mathbf{X}, t) \cdot \nabla_{\mathbf{X}} I(\mathbf{X}, t) &= -A(\mathbf{X}, t) I(\mathbf{X}, t) \quad \mathbf{X} \in \mathcal{B}_0 \\ I(\mathbf{X}, t) &= I_0(\mathbf{X}, t) \quad \mathbf{X} \in \partial \mathcal{B}_0 \end{aligned} \quad (6)$$

where  $A$ ,  $\mathbf{l}$ ,  $I_0$  are the material's absorptivity, the unit vector of the incoming light beam and the known intensity of light on the boundary of the domain (Fig. 3). When a simple 1D light diffusion in a medium with constant absorbance is considered, the light intensity decays exponentially within the body as:

$$I(z, t) = I_0(t) \exp(-Az) \quad (7)$$

Once the light intensity in the domain has been determined, the generated heat density per unit time is provided by [23]:

$$q_G(\mathbf{X}, t) = A(\mathbf{X}, t) I(\mathbf{X}, t) \quad \mathbf{X} \in \mathcal{B}_0 \quad (8)$$

where high values of  $A$  provide an increase in the generated heat but hinder the light diffusion, resulting in a reduction of the light intensity in the domain. The absorbance of mixing comes from the contributions of the gel, the embedded particles (with molar absorptivity  $\theta$ ) and the fluid. The following expression has been proposed:

$$A(\mathbf{x}, t) = \theta \frac{C_n(\mathbf{X})}{J(\mathbf{X}, t)} + A_{net} \frac{1}{J(\mathbf{X}, t)} + A_{fluid} \left[ \frac{J(\mathbf{X}, t) - 1}{J(\mathbf{X}, t)} \right] \quad (9)$$

in the current deformed configuration, while in the reference one  $A(\mathbf{X}, t) = A(\mathbf{x}, t) J^{1/3}(\mathbf{X}, t)$  [23].

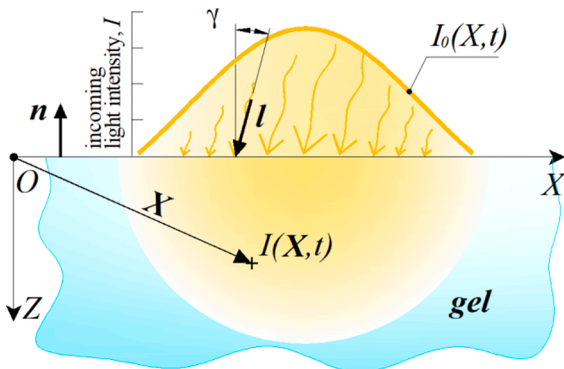


Fig. 3. Light diffusion within a semitransparent medium.

### 3. Micromechanics of a polymer network

The deformational energy of the polymer can be described by a micromechanical model that accounts for the arrangement of polymer chains. In fact, it has been well established that, thanks to the amorphous character of the polymer network made of an entangled arrangement of chains, the material is mainly characterized by an entropic energy which can be quantified by the knowledge of the network's spatial configuration.

Within this framework, it is standard to assume that each chain is made of  $N$  rigid (Kuhn's) segments of equal length  $b$  whose physical state, according to the FJC assumption, depends only on the chain's end-to-end vector  $\mathbf{r}$  [24]. The chains form a solid since they are reciprocally linked at discrete points (cross-links) to form a 3D structure. In the stress-free state, the chain statistical distribution  $\rho_0(\mathbf{r})$  in the 3D chain network space (microscale) – related to the continuum scale (macro-scale) by means of the affine deformation hypothesis – is usually assumed to obey the standard Gaussian distribution  $\phi_0$  in the form  $\rho_0(\mathbf{r}) = c_a \phi_0(\mathbf{r})$ , where  $c_a$  is the cross-link density [25]. Once the function  $\rho_0$  is known, the free energy density of the gel in a generic deformed state, characterized by the chain statistical distribution  $\rho(\mathbf{r})$ , can be evaluated as:

$$\begin{aligned} \Delta \Psi_{gel} &= \Delta \Psi_{net} + \Psi_{mix} \quad \text{where} \\ \Delta \Psi_{net} &= \Psi_{net} - \Psi_{net,0} = \int_{\Omega} [\rho(\mathbf{r}, t) - \rho_0(\mathbf{r})] \psi(\mathbf{r}) d\Omega \end{aligned} \quad (10)$$

where  $\psi(\mathbf{r})$  is the energy per chain. The above difference account for the non-zero energy of the stress-free state of the network. By adopting the simplest Gaussian statistics model to express the energy in a single chain,  $\psi(\mathbf{r}) = (3k_B T / 2Nb^2) |\mathbf{r}|^2$ , and by defining the distribution tensors  $\delta = \langle \phi \mathbf{r} \otimes \mathbf{r} \rangle$ ,  $\delta_0 = \langle \phi_0 \mathbf{r} \otimes \mathbf{r} \rangle$  (i.e. the covariance tensors of the distribution of  $\mathbf{r}$  in the deformed and undeformed states, respectively, with  $\langle \mathbf{r} \otimes \mathbf{r} \rangle = \int_{\Omega} \mathbf{r} \otimes \mathbf{r} d\Omega$ ),  $\Delta \Psi_{gel}$  becomes [25]:

$$\Delta \Psi_{gel} = \frac{3c_a k_B T}{2Nb^2} \text{tr}(\delta - \delta_0) + \pi [J - \bar{J}] \quad (11)$$

being  $J = \det \mathbf{F}$ ,  $\bar{J} = 1 + C_s v_s$ , the volume ratio of the material and the actual volume ratio of the gel with respect to the initial dry state of the polymer, respectively.

Finally, the macroscopic true stress state in the material can be easily shown to be given by the following expressions [25]

$$\boldsymbol{\sigma} = J^{-1} \mathbf{P} \mathbf{F}^T = \underbrace{\frac{3c_a k_B T}{Nb^2} (\delta - \delta_0)}_{\boldsymbol{\sigma}_{net}} - \underbrace{\pi \mathbf{1}}_{\boldsymbol{\sigma}_{mix}}, \quad \mathbf{P} = \frac{\partial \Delta \Psi_{gel}}{\partial \mathbf{F}}. \quad (12a)$$

$$\text{or } \boldsymbol{\sigma} = \left\langle c_a [\phi(\mathbf{r}, t) - \phi_0(\mathbf{r})] \frac{\partial \psi}{\partial \mathbf{r}} \otimes \mathbf{r} \right\rangle - \pi \mathbf{1} \quad (12b)$$

where  $\boldsymbol{\sigma}_{net}$  is the elastic stress obtained by averaging the forces  $\mathbf{f} = \partial \psi / \partial \mathbf{r}$  of the network's chains. The hydrostatic mixing Cauchy stress  $\boldsymbol{\sigma}_{mix}$  is given by:

$$\begin{aligned} \boldsymbol{\sigma}_{mix} &= -J^{-1} \frac{\partial \Psi_{mix}}{\partial \mathbf{F}} \mathbf{F}^T = -J^{-1} \frac{\partial \Psi_{mix}}{\partial J} \frac{\partial J}{\partial \mathbf{F}} \mathbf{F}^T \\ &= \frac{k_B T}{v_s} \left[ \frac{1}{J} + \frac{\chi}{J^2} + \ln \left( \frac{v_s C_s}{J} \right) \right] \mathbf{1} \end{aligned} \quad (13)$$

being  $\partial J / \partial \mathbf{F} = J \mathbf{F}^{-T}$ . The mixing stress is represented in dimensionless form in Fig. 4; it can be appreciated that, for a given stress state in the network, the amount of fluid present in the gel is greater for lower value of the parameter  $\chi$ , here assumed to be not dependent on the volume rate  $J$  or on the temperature. If no external actions are applied to the material, the equilibrium equation  $\nabla \cdot \boldsymbol{\sigma} = \mathbf{0}$  must be satisfied pointwise by the Cauchy stress tensor, and so  $\boldsymbol{\sigma}_{net} = -\boldsymbol{\sigma}_{mix}$ , indicating that the fluid is

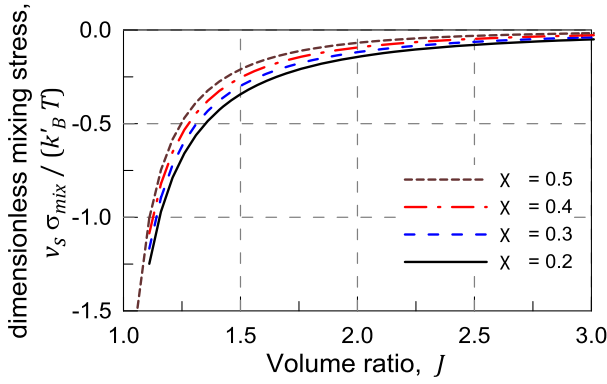


Fig. 4. Mixing stress vs volume ratio  $J$  for various values of the Flory-Huggins interaction parameter.

under a compressive hydrostatic stress state and the polymer network undergoes the same pressure with positive sign, i.e. the network chains are under tension.

### 3.1. Response of a one-dimensional temperature-dependent gel

In order to illustrate the response of a hydrogel that swells and is subjected to an external force, let us consider a pNIPAm hydrogel (shear modulus  $G = 1.4 \text{ MPa}$  and  $T_{LH} = 305 \text{ K}$ , with the interaction parameter  $\chi(J, T)$  described by Eq. (4)), which is initially free to swell ( $0 \leq t \leq t_1$ ) and then stretched along the direction  $X_1$  by applying the deformation history  $\lambda_1(t)$  (see Fig. 5 and the deformation profiles in Fig. 6a and Fig. 7a). A slow deformation rate, corresponding to a quasi-static loading, is applied to the hydrogel.

The evolution in time of the applied stresses and those arising in the network as well the volume ratio  $J$  of the gel at the constant temperatures  $T = 303 \text{ K}$  and  $T = 308 \text{ K}$  are illustrated in Fig. 6b and Fig. 6c, respectively, where the free swelling phase is followed by a tensile cycle characterized by a maximum stretch of  $\lambda_1 = 2.0$ . The bar is assumed to be restrained at its left hand extremity with respect to the displacement along  $X_1$  only. Firstly, free swelling is allowed to occur; during this phase, the network freely expands in the three Cartesian directions, and thus the polymer chains result to be isotropically stretched. Correspondingly, in order to have a zero global stress state, the fluid entering into the network results to be compressed by the same amount. After free swelling, a mechanical deformation is imposed to the gel along the direction  $X_1$ , starting from the stretch value reached at the end of the free swelling. For a pNIPAm gel, the latter value depends on the temperature at which the test is performed (see Figs. 6, 7). It is worth mentioning that in real applications it is important the knowledge of the stress state arising in the solid phase (i.e. in the network). From this perspective, the micromechanical model summarized by Eqs (10)-(13), clearly outlines the solid-fluid interplay. However, for sake of completeness we also report the stress applied externally to the bar during mechanical deformation.

It can be easily appreciated that when free swelling occurs below  $T_{LH}$ , the gel absorbs a huge amount of fluid and the network is highly stretched; during mechanical loading, the stress increases along the

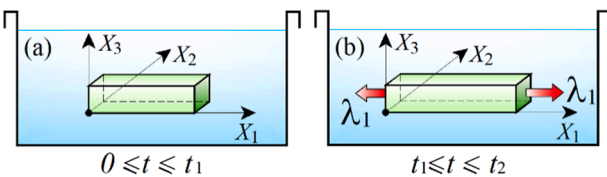


Fig. 5. Gel undergoing free swelling (a) and subsequently stretched along the direction  $X_1$  while maintained in contact with the solvent (b).

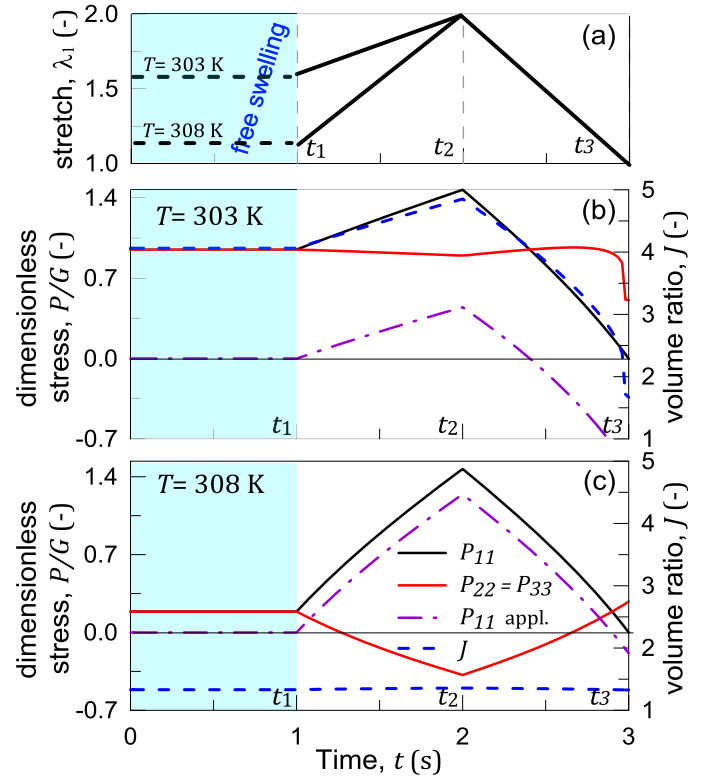


Fig. 6. Applied tensile stretch history  $\lambda_1(t)$  (a). Nominal stresses arising in the solid fraction of the gel ( $P_{11}$ ,  $P_{22}$ ,  $P_{33}$ ), for a temperature-sensitive hydrogel undergoing free swelling followed by an imposed mechanical deformation cycle at  $T = 303 \text{ K}$  (b) and  $T = 308 \text{ K}$  (c).

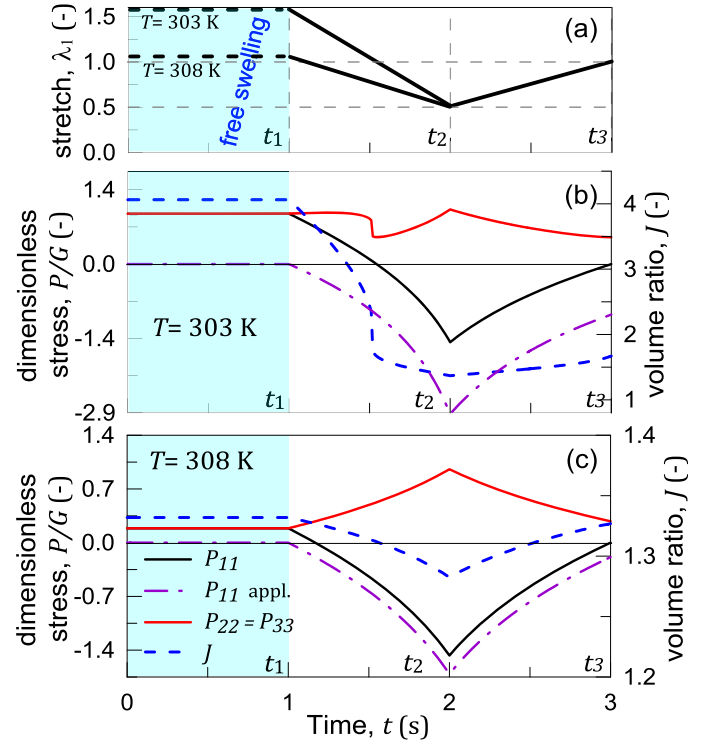


Fig. 7. Applied compression stretch history  $\lambda_1(t)$  (a). Nominal stresses arising in the solid fraction of the gel ( $P_{11}$ ,  $P_{22}$ ,  $P_{33}$ ), stress applied to the gel bar ( $P_{11}$  appl.), and volume ratio  $J$  for a temperature-sensitive hydrogel undergoing free swelling followed by a mechanical compressive cycle at  $T = 303 \text{ K}$  (b) and  $T = 308 \text{ K}$  (c).



stretch direction and slightly reduces in the others due to the high amount of fluid permeating the network (stretched chains improve the fluid permeation) (Fig. 6b).

On the other hand, when  $T > T_{LH}$  the gel has a low affinity with the fluid and the volume ratio is just a bit higher than 1.0; during mechanical loading and unloading, the volume ratio is very limitedly influenced by the stretch and the gel behaves similarly to a dry material (Fig. 6c).

Fig. 7 shows the response of the temperature sensitive hydrogel, after free swelling is allowed to occur, when it is subjected to a compression cycle (minimum value of the applied stretch  $\lambda_1 = 0.5$ ). If the case  $T = 303K < T_{LH}$  is considered, free swelling leads to a volume change of about  $J = 4$ ; compressing the material forces the fluid to exit the network, leading to a volume ratio  $J \cong 1.5$  for  $\lambda = 0.5$ , while stretching back to the undeformed state ( $\lambda = 1$ ) allows the fluid to enter again in the network leading to  $J \cong 1.7$ . This happens because of the constraint imposed by the applied axial deformation that does not allow the material to expand by swelling along  $X_1$  (Fig. 7b). When the material has a bad affinity with the fluid (i.e. at  $T = 308K > T_{LH}$ ), swelling is quite limited and compressive deformation induces a small amount of fluid to exit from the network (Fig. 7c).

These simple examples show how big can be the difference of the response of a pNIPAm hydrogel by varying its temperature. This suggests that using the temperature as a tuning stimulus to control the fluid entering or exiting from the gel, can be an effective way of changing in a controlled way the deformation of the material without the need to apply a mechanical deformation.

#### 4. Multi-physics involved in light-driven responsiveness of temperature-sensitive hydrogels

As shown above, the fluid uptake is responsible for the volume change of the polymer network; this affects the physical properties of the mixing (such as thermal properties, mass density, etc.) and the overall light absorbance of the material. Consequently, the light-induced temperature variation within the material and the FH parameter are influenced by the swelling itself. This provides an intriguing interplay of different mechanisms that can be exploited for obtaining a tunable swelling. The temperature field arising because of the photo-thermal heating induced by light radiation, coupled with the swelling phenomenon, is here evaluated by solving the standard heat conduction equation (equipped with the related boundary conditions):

$$-\nabla \cdot [k_{gel}(X, t) \nabla T(X, t)] + \rho_{gel}(X, t) c_{p, gel}(X, t) \frac{\partial T(X, t)}{\partial t} = q_G(X, t) - q_L(X, t) \quad (14)$$

where the right-hand side of Eq. (14) is the specific heat (generated and dispersed, respectively) per unit time. When the photo-thermal effect is considered, the generated heat is expressed as  $q_G = A(X, t)I(X, t)$  (see sect. 2.3), while the heat loss is assumed to be quantified as  $q_L = c_L[T(X, t) - T_r]$ , where  $c_L$  is a property of the material quantifying the amount of heat dispersed per unit time and per unit temperature difference and  $T_r$  is the initial (reference) temperature. In Eq. (14),  $k_{gel}$ ,  $\rho_{gel}$  and  $c_{p, gel}$  are physical properties of the gel, namely the thermal conductivity, mass density and specific heat, respectively. These properties can be conveniently evaluated accounting for the volume fractions of the fluid (subscript 'fluid') and of the polymer network (subscript 'net') by adopting the mixing rule:

$$\begin{aligned} k_{gel}(X, t) &= \frac{[k_{net} + (J - 1)k_{fluid}]}{J} \\ \rho_{gel}(X, t) &= \frac{[\rho_{net} + (J - 1)\rho_{fluid}]}{J} \\ c_{p, gel}(X, t) &= \frac{[c_{p, net} + (J - 1)c_{p, fluid}]}{J} \end{aligned} \quad (15)$$

Being  $J = J(X, t)$ , all the above quantities are space- and time-dependent.

#### 5. Numerical simulations

##### 5.1. Light-driven controlled swelling

The mechanical response in presence of light-radiation and cooling of a cubic domain ( $L = H = t = 1$  mm) made of a thermo-responsive hydrogel is considered hereafter. The body is made of pNIPAm hydrogel with embedded photo-thermal particles (2.3% in weight,  $C_n(X) = 99.8 \text{ mol/m}^3$ ). A simple 2D plane stress model is adopted, whereas a regular mesh of  $10 \times 10$  4-noded elements is used for the discretization. The body is assumed to be restrained at its bottom edge only: the central point lying on its bottom edge is fixed ( $u_x = u_y = 0$ ), while the remaining points on the bottom edge are free to slide on a horizontal plane ( $u_y = 0$ ).

The physical properties of the hydrogel are assumed to be as follows: Young modulus  $E = 1 \text{ kPa}$ ,  $\nu = 0.5$ , mass density  $\rho_{net} = 1000 \text{ kg/m}^3$ , thermal conductivity  $k_{net} = 0.2 \text{ W/mK}$  and specific heat  $c_{p, net} = 1050 \text{ J/kgK}$ . The fluid permeating the gel has mass density  $\rho_{fluid} = 1000 \text{ kg/m}^3$ , molar volume and thermal conductivity  $v_s = 1.8 \cdot 10^{-5} \text{ m}^3/\text{mol}$ ,  $k_{fluid} = 0.5 \text{ W/m K}$ , while the diffusivity is  $D = 10^{-7} \text{ m}^2/\text{s}$  and  $C_p = 4000 \text{ J/kgK}$ .

The interaction parameter, evaluated according to Eq.(5) ( $\chi_b$ ), has been assumed to follow the expression reported in [9] (see sect. 2.2), by adopting  $\chi_L = 0.2$ ,  $\chi_H = 2$ ,  $T_{LH} = 304 \text{ K}$  and  $c = 5 \text{ K}$ . The absorbance is evaluated by adopting Eq. (9), assuming  $A_{net} = 800 \text{ m}^{-1}$ ,  $A_{fluid} = 0 \text{ m}^{-1}$  and  $\theta = 20 \text{ m}^2/\text{mol}$ ; when the material is in the stress-free state (undeformed configuration,  $J = 1$ ,  $T = T_r$  reference temperature), from Eq. (9) we get  $A_0 = 2796 \text{ m}^{-1}$ ; this value will be used in the following to define the dimensionless quantities.

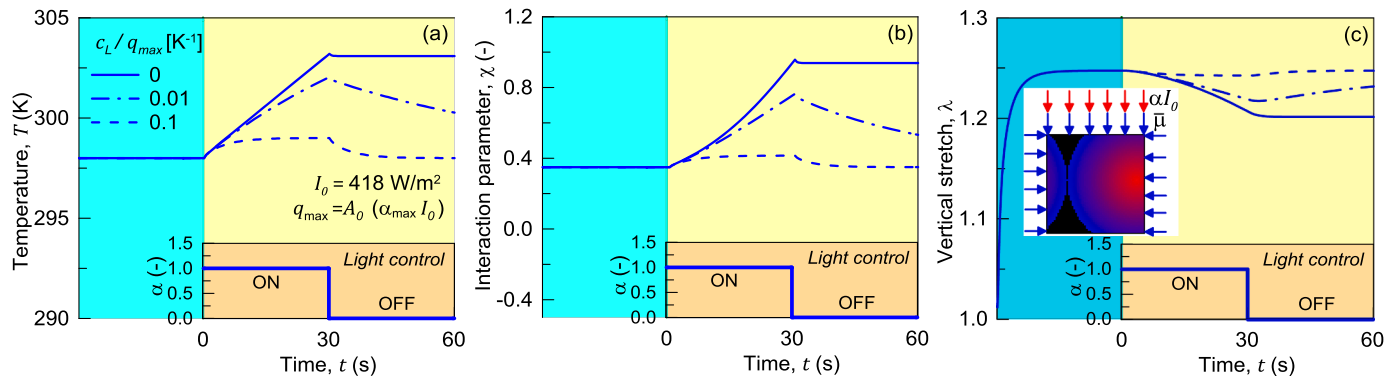
The simulation considers free swelling without any external stimulus in the time interval ranging from  $t = -30 \text{ s}$  to  $t = 0 \text{ s}$  (the left, top and right edges of the material domain are in contact with the fluid), while a uniform light radiation  $I(X, t) = \alpha(t)I_0$  with  $I_0 = 418 \text{ W/m}^2$ , is assumed to be spread on the top of the domain during the following 30 s, i.e. during the time interval  $t = 0 - 30 \text{ s}$ , in which  $\alpha(t) = 1$  (Fig. 8). Finally, the light is turned off within the interval  $t = 30 - 60 \text{ s}$ ,  $\alpha(t) = 0$ .

In order to investigate how cooling the material affects the material responsiveness, the material is assumed to lose heat energy: three values of the heat loss intensity  $c_L/q_{max}$  are considered, namely  $c_L/q_{max} = 0$ ; 0.01; 0.1. It is worth mentioning that the quantity  $q_{max} = A_0(\alpha_{max}I_0)$  has been introduced for evaluating the energy loss in dimensionless form, being  $A_0$  the material absorbance of the dry polymer and  $\alpha_{max}$  the maximum value of the multiplicative factor taking place during the light time history ( $\alpha_{max} = 1$ , in the particular example here considered).

The temperature and the interaction parameter at the central point of the top edge of the domain vs time are illustrated in Fig. 8a,b, whereas the vertical stretch of the material is plotted in Fig. 8c for the three above-mentioned values of  $c_L/q_{max}$ .

If the material cooling is neglected ( $c_L/q_{max} = 0$ ), the temperature increases and remains constant after turning off the light (continuous line in Fig. 8a); correspondingly, the interaction parameter firstly increases and then remains constant (continuous line in Fig. 8b). As a consequence, the stretch reduces since the fluid concentration decreases due to the increase of the FH parameter (lower solid-fluid affinity), until an equilibrium configuration is attained ( $\lambda \cong 1.2$ , continuous line in Fig. 8c) when the light is turned and kept off.

The material response becomes different if cooling occurs. When the highest value of the dimensionless coefficient of heat dispersion is considered ( $c_L/q_{max} = 0.1$ ), the temperature slightly increases upon light irradiation (dashed line in Fig. 8a) and slightly reduces when the light is turned off; as a consequence, the interaction parameter remains almost identical to the initial value  $\chi_L$  (dashed line in Fig. 8b). The fluid concentration remains practically unchanged as well as the stretch ( $\lambda \cong 1.25$ , dashed line in Fig. 8c). In this latter case, because of the interplay between the generated and dispersed heat,  $q_G(X, t)$  and  $q_L(X, t)$ ,



**Fig. 8.** Light-driven deformation of a thermo-responsive hydrogel, under swelling, subjected to photo-thermal heating and self-cooling. Three values of the dimensionless heat loss per unit time,  $c_L/q_{max} = 0; 0.01; 0.1$ , are considered. The temperature variation (a), the interaction parameter (b), and the vertical stretch (c) of the material vs time are illustrated.

light-induced heating is not effective in modifying the responsiveness of the material.

Finally, the case with  $c_L/q_{max} = 0.01$  is considered; compared with the case  $c_L/q_{max} = 0.1$ , the temperature increases faster when the light is on; however, when the light is turned off, the temperature decreases faster (dash-dot line in Fig. 8a), being the heat loss proportional to the current temperature of the material, i.e.  $q_L(\mathbf{X}, t) \propto T(\mathbf{X}, t)$ , greater with respect to the case  $c_L/q_{max} = 0.01$  rather than for  $c_L/q_{max} = 0.1$ . As far as the interaction parameter is concerned, it firstly increases and then decreases when the light is turned off (dash dot line in Fig. 8b). When the light is turned off, further swelling occurs because of the decrease in temperature due to cooling, responsible for a decrease of the FH parameter. This corresponds to an expansion of the material whose stretch tends to that of the initial free-swelling state ( $\lambda \cong 1.25$ ,  $t = 0$  s), which is asymptotically attained when the temperature returns to the initial reference one,  $T(\mathbf{X}, t) = T_r$ .

## 6. Conclusions and future developments

In the present study we have considered the mechanical response of temperature-sensitive hydrogels by introducing a multi-physic model accounting for the various physical phenomena involved, namely heat generation and conduction, light diffusion, and mechanics of swelling. This class of gels with controllable swelling is relevant to several advanced applications, enabling making untethered sensors and actuators. Thanks to their biocompatibility and because their stimuli-controlled physical properties and high-water content, are quite similar to those of natural living tissues, these gels are perfect candidates for several applications in bio-related fields. We have considered a specific class of gels, namely poly-N-isopropylacrylamide (pNIPAm) hydrogels whose affinity with the fluid changes severely with the temperature. Thanks to their semi-transparency, the photo-thermal effect can be adopted to heat up the material and to change its network-fluid interaction parameter. Simple cases of swelling taking place in presence of a temperature variation has been considered to demonstrate the effect of a temperature change in the mechanical deformation of the material. Cooling has also been considered to occur and its role in self-deformation capabilities has been discussed.

The swelling-stretching interplay has been considered for a simple case of a gel element subjected to tensile or compressive stretching, while a more complex example consisting in determining the response of a gel under cycles of light spread to the material has been examined. A variety of responses arises by controlling the temperature field in the gel; this opens new perspectives in the design of responsive devices stimulated by heat or by light sources.

However, several aspects need to be further considered to describe more precisely the phenomena involved in temperature-driven gels,

such as heat diffusion due to the fluid flow under large deformation, light diffusion in an evolving domain as well as more complex boundary conditions. PNIPAm hydrogels have a soft architectural structure and relatively high solvent swelling: these are desirable features in certain applications (cells encapsulations, drug delivery, etc.) where both soft viscoelastic behavior and large amount of water uptake are required [26]. On the other hand, the low polymer density in the swollen state is one of the reasons of poor mechanical properties in PNIPAm hydrogels [27] which could hinder their use in applications requiring superior mechanical properties. However, the peculiarities of PNIPAm hydrogel structure allows the material properties to be easily tuned: several approaches (interpenetrating polymer network, copolymerization, slide-ring hydrogels development, etc.) have widen the possibility of improving the mechanical properties of PNIPAm [26–27]. Within this context, the comprehensive physics-based model presented, enables a precise design of gel-based devices, whose response can be tuned at will according to the application of interest.

## Declaration of Competing Interest

None.

## Data availability

Data will be made available on request.

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