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Light intensity controlled wrinkling patterns in photo-thermal sensitive hydrogels

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Abstract. Undergoing large volumetric changes upon incremental environmental stimulation, hydrogels are interesting materials which hold immense potentials for utilization in a wide array of applications in diverse industries. Owing to the large magnitudes of deformation it undergoes, swelling induced instability is a commonly observed sight in all types of gels. In this work, we investigate the instability of photo-thermal sensitive hydrogels, produced by impregnating light absorbing nano-particles into the polymer network of a temperature sensitive hydrogel, such as PNIPAM. Earlier works have shown that by using lights of different intensities, these hydrogels follow different swelling trends. We investigate the possibility of utilizing this fact for remote switching applications. The analysis is built on a thermodynamic framework of inhomogeneous large deformation of hydrogels and implemented via commercial finite element software, ABAQUS. Various examples of swelling induced instabilities, and its corresponding dependence on light intensity, will be investigated. We show that the instabilities that arise have their morphologies dependent on the light intensity.

Keywords: dual-sensitive; photo-thermal sensitive hydrogel; bifurcation; buckling; instability

1. Introduction

Instabilities exist widely in various types of hydrogels due to the large deformation that is involved when a gel is placed in contact with a stimulus. Some examples of commonly seen instabilities are bilayer structures, where a film is attached to a thicker substrate of different material properties (Sun *et al*. 2011, Yang *et al*. 2010), surface instabilities through either wrinkling or creasing (Barros *et al*. 2012, Guvendiren *et al*. 2009, Toh *et al*. 2015, Trujillo *et al*. 2008, Yoon *et al*. 2012), bulk buckling of constrained gels (DuPont Jr *et al*. 2010, Lee *et al*. 2012, Liu *et al*. 2010, Liu *et al*. 2011, Mora and Boudaoud 2006) and bifurcation of gels with periodic patterns (Wu *et al*. 2014).

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Once considered an undesirable trait, the potentials of harnessing instabilities into useful applications has fueled much research interest recently, providing promising utilizations such as microfluidics, tunable adhesion and microarrays (Chen and Yang 2012, Kang *et al*. 2013). One phenomenon which has garnered much interest in recent times is the bifurcation of gel layers with holes arranged in a periodic manner (Bertoldi *et al*. 2008, Mullin *et al*. 2007, Okumura *et al*. 2015, Okumura *et al*. 2014) due to the pattern transformation that arises in an ordered arrangement.

On the other hand, photo-thermal sensitive hydrogels are a suitable class of material for the many potential applications due to its fast response (Suzuki and Tanaka 1990) and also the ability to be controlled remotely (Sershen *et al*. 2000). In this paper, we study the effects of irradiation intensity and arrangement of different rows of holes on a photo-thermal sensitive hydrogel. The potential of light as a viable controlling method to trigger sudden change in geometry in soft structures is explored. This is done by utilizing the finite element model we recently developed (Toh *et al*. 2014) to simulate the bifurcation process.

The paper is arranged as such: Section 2 briefly describes the thermodynamic model and finite element implementation of a photo-thermal sensitive gel, developed earlier by (Toh *et al*. 2014). In Section 3, we apply the finite element model to develop numerical models and simulate the bifurcation of photo-thermal sensitive gel structures under various loading and geometrical conditions before wrapping up in Section 4.

2. Thermodynamic theory of a photo-thermal sensitive hydrogel

2.1 Thermodynamic equilibrium

In the large deformation theory of a polymeric gel, the loads that a gel experiences are external mechanical loads, represented by a body force B_i and traction T_i, and chemical potential of μ^s due to exposure to an external solvent. For such a gel with additional light-absorbing nano-particles incorporated in the network, there is an additional load due to the irradiation of light, represented by a chemical potential of photo-chemical reactions occurring in the nano-particles μ^p. In equilibrium, the change in free energy W of the system is balanced by these external loads

$$\int \delta W dV = \int B_i \delta x_i dV + \int T_i \delta x_i dS + \mu^s \int \delta C^s dV + \mu^p \int \delta C^p dV \tag{1}$$

Performing a Legendre transformation, we introduce a new free energy function, $\hat{W} = W - \mu^s C^s - \mu^p C^p$. The primary objective of this transformation, as elaborated in (Ding *et al*. 2013, Hong *et al*. 2009, Toh *et al*. 2014), is to convert the equilibrium Eq. (1) into a hyperelastic solid equilibrium equation,

$$\int \delta \hat{W} dV = \int B_i \delta x_i dV + \int T_i \delta x_i dS \tag{2}$$

2.2 Constraint equations

In the deformation of a photo-thermal sensitive hydrogel, the stress present in the gel does not cause significant volumetric change to constituent polymer and solvent particles due to the small order of magnitude. As a consequence, we impose the incompressibility constraint on the gel, which is commonly written in the form

$$1+\nu C^{s}=\det\mathbf{F} \tag{3}$$

In addition, the increase in temperature of the gel follows conservation of energy and this constraint, after simplification, can be written as

$$C^{p}=\left[\frac{c_{v}^{w}}{J}+\frac{c_{v}^{network}-c_{v}^{w}}{J^{2}}\right]\frac{\alpha I_{0}}{\hbar f} \tag{4}$$

where c_v^w and $c_v^{network}$ are the volumetric heat capacity of water and the polymer network respectively, α is a proportionality constant, and $\hbar f$ the energy of a single photo-chemical reaction.

2.3 Specialization of free energy function

Applying constraint equations of incompressibility and energy conservation, together with the Flory-Rehner theory, the modified free energy function can be expressed as

$$\begin{aligned}\hat{W}=&\frac{1}{2}Nk_{B}T\left[J^{\frac{2}{3}}\bar{I}_{1}-3-2\ln\left(J\right)\right]+\frac{k_{B}T}{\nu}\left(J-1\right)\left[\ln\left(\frac{J-1}{J}\right)+\left(\frac{\chi_{0}}{J}+\frac{\chi_{1}}{J^{2}}\right)\right]\\&-k_{B}T\frac{\alpha I_{0}}{hf}\left[\left(c^{(p)}-c^{(w)}\right)\left(\frac{1}{J^{2}}\right)+c^{(w)}\left(\frac{1}{J}\right)\right]-\mu\left(\frac{J-1}{\nu}\right)\end{aligned} \tag{5}$$

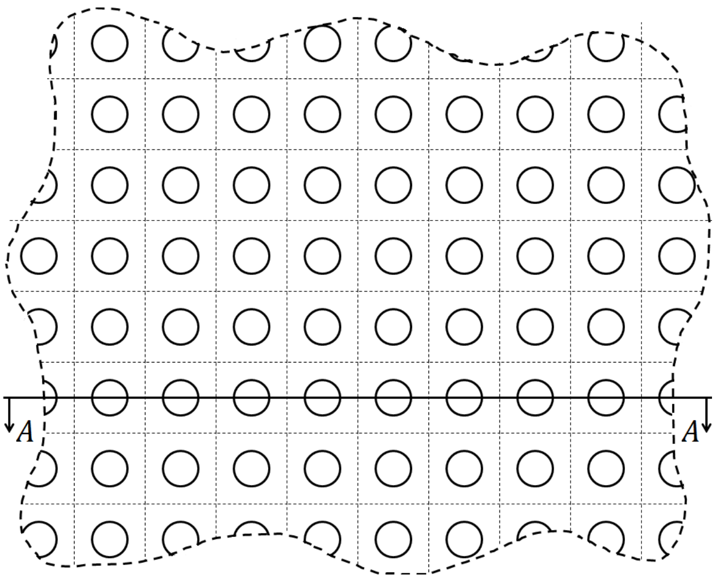
Under this new definition, the nominal stress experienced in the gel derived to be

$$\begin{aligned}s_{iK}=&\frac{\partial\hat{W}}{\partial F_{iK}}\\=&Nk_{B}T\left(F_{iK}-H_{iK}\right)+\frac{k_{B}T}{\nu}\left[\ln\left(\frac{J-1}{J}\right)+\frac{1}{J}+\frac{\chi_{0}-\chi_{1}}{J^{2}}+\frac{2\chi_{1}}{J^{3}}\right]JH_{iK}\\&+k_{B}T\frac{\alpha I_{0}}{\hbar f}\left[\left(c^{(p)}-c^{(w)}\right)\frac{2}{J^{3}}+c^{(w)}\left(\frac{1}{J^{2}}\right)\right]JH_{iK}-\frac{\mu}{\nu}JH_{iK}\end{aligned} \tag{6}$$

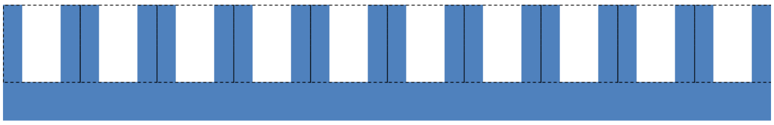
3. Numerical modeling

The finite element implementation of a photo-thermal sensitive hydrogel can be achieved either of the two Abaqus subroutines: UHYPER (Ding *et al*. 2013, Hong *et al*. 2009, Marcombe *et al*. 2010, Toh *et al*. 2014) or UMAT (Kang and Huang 2010). For this work, we adopt the UHYPER model developed by (Toh *et al*. 2014).

3.1 Pattern transformation in a gel layer with period hole array



(a)



(b)

Fig. 1 (a) Top view of the gel layer with periodic square array of holes, (b) cross section view of section A-A

In an extensive gel film fixed at the bottom and having periodic array of holes, as shown in Fig. 1, swelling of the gel causes instabilities in the form of rotation of unit cells to form slits with periodic patterns, such as alternating slits which are perpendicular to each other.

In the finite element model, the simplest repeating unit consists of a square with a circle in the middle. However, this repeating unit does not allow for appearance of alternating slits and we make use of $m \times n$ repeating units to form the unit cell for simulation, upon which we apply periodic boundary conditions, where displacements of opposite sides are equal. Imposition of periodic boundary condition is done by using the *EQUATION option. For computational efficiency, we make use of plane stress elements to perform two-dimensional analysis on the pattern formation in the gel structure.

3.1.1 Effects of light intensity on bifurcation process

In studying the effects of light intensity, we turn our focus to a square repeating unit. As reported by (Okumura *et al*. 2015, Okumura *et al*. 2014), for a gel with a square array of holes, a minimum of 2×2 repeating units are required to form the unit cell, as shown in Fig. 2.

We first subject a gel of initial chemical potential of $\bar{\mu} = -0.2$ in the stress free state to a final chemical potential of $\bar{\mu} = 0$. As swelling occurs, the holes remain circular in the initial period. However, across a critical chemical potential, bifurcation sets in and there is rotation in the middle of the four holes, as indicated in the diagram. Due to this rotation, the holes transit into alternating slits, as shown in Fig. 3.

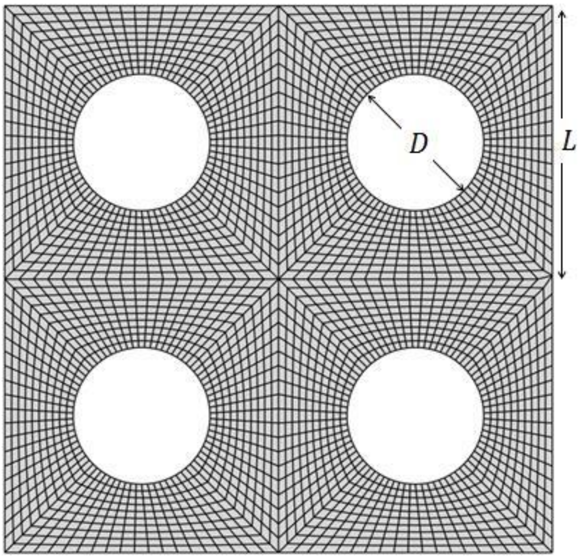


Fig. 2 Mesh of unit cell of 2×2 repeating units of length L=1.5 and diamter D=0.75

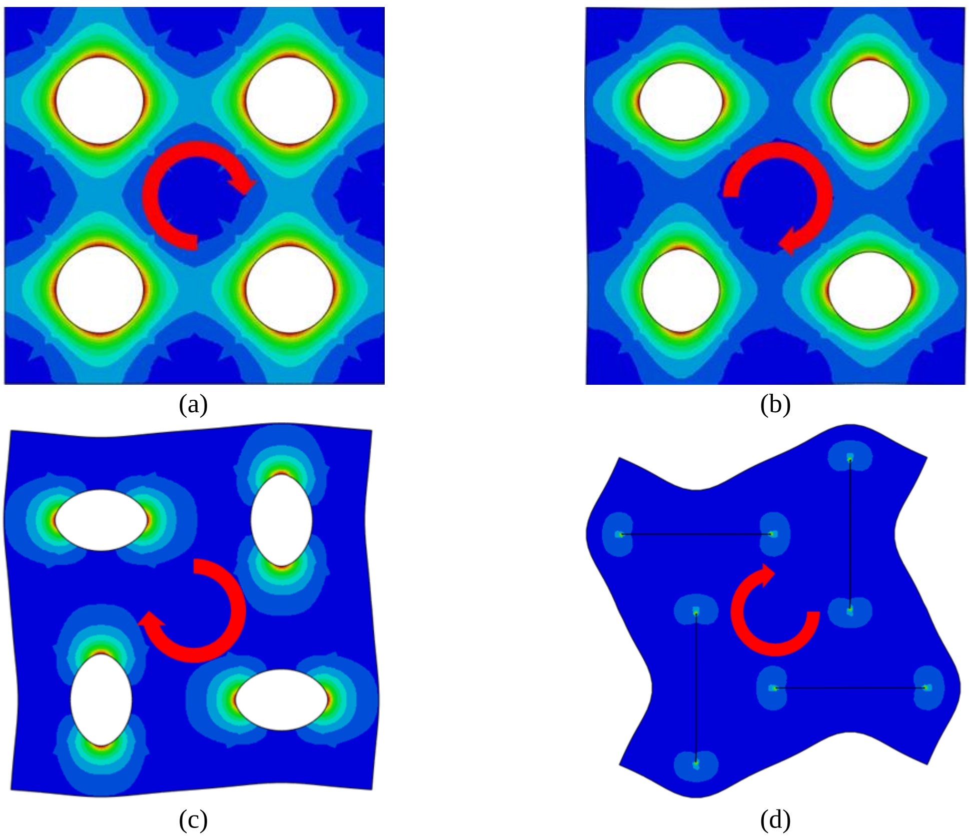


Fig. 3 Transition of holes into slits at chemical potentials at (a) $\bar{\mu}=-0.1$, (b) $\bar{\mu}=-0.053$, (c) $\bar{\mu}=-0.052$ and (d) $\bar{\mu}=0$. The red arrows indicate direction of rotation of the middle of the unit cell. Contours show the non-dimensionalized Mises stress

To quantify the amount of deviation from the original circular geometry, we calculate the eccentricity of the slit, given by $e=\sqrt{1-\left(\frac{a}{b}\right)^2}$, with *a* and *b* being the semi-minor and semi-major axes. Under this definition, *e*=0 when the hole is a perfect circle, and becomes *e*=1 as the elongation of this hole propagates.

In this example, we propose an optical switch which utilizes the ON-OFF geometry of the slits. We first hydrate a dry gel which is in a square array (Fig. 5(a)). This hydration causes swelling and eventually bifurcation into the arrangement with alternating slits (Fig. 5(b)), which we set as the normal OFF state. When we apply an irradiation, the gel gains temperature and undergoes deswelling. This deswelling action allows the gel to return to circular arrangement (Fig. 5(c)) (OFF state).

In this swollen state, we subject the gel to irradiation of different intensities, which all cause a temperature change in the gel, thus causing the gel to deswell and undo the effects of bifurcation, returning the geometry of the slits into circles. Fig. 6 shows the eccentricities of gels which are exposed to different levels of light intensity. There is a clear distinction of the critical transition temperatures as light intensity is increased.

Plotting this relationship between light intensity and the critical temperature, we obtain a linear relationship between critical temperature and light intensity. The clear distinction of critical temperatures of bifurcation indicates potential applications in areas of optical switching or microfluidics, as the opening and closing of the holes can be precisely controlled with different light intensities.

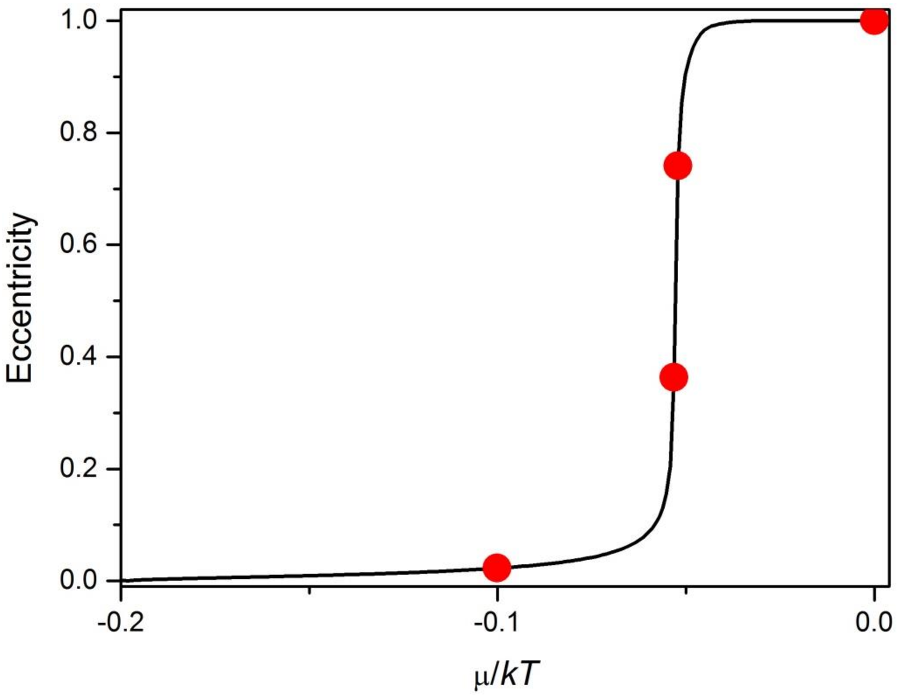


Fig. 4 Change in eccentricity of the gel structure as chemical potential is changed from $\bar{\mu}=-0.2$ to $\bar{\mu}=0$. The four discrete points correspond to swelling states illustrated in Fig. 6

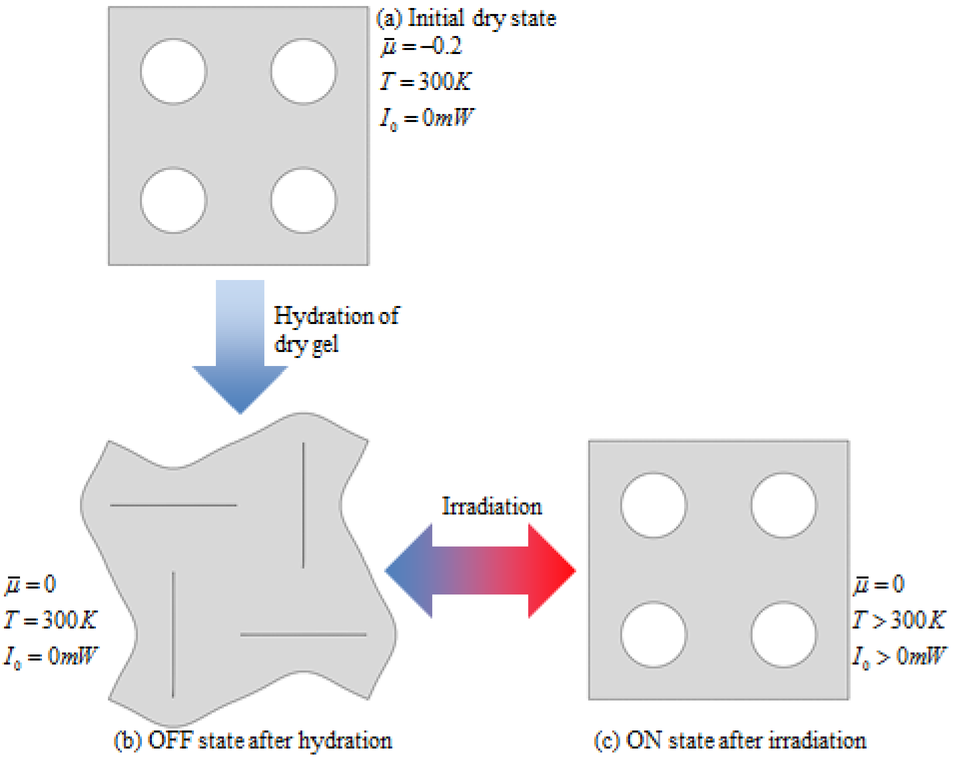


Fig. 5 Geometry of (a) initial dry state, (b) swollen state with no irradiation, (c) gel returns to circular geometry under irradiation

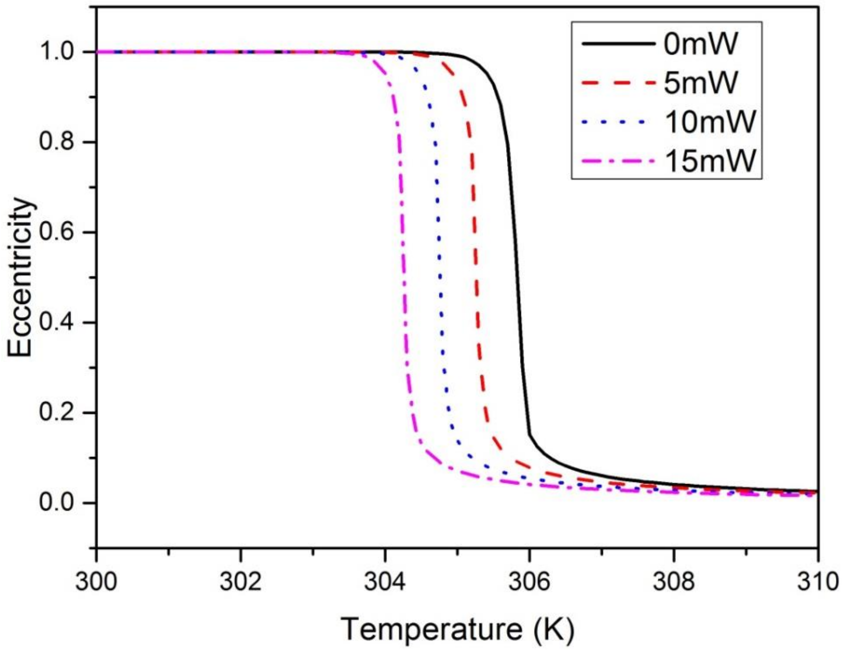


Fig. 6 Dependence of eccentricity with temperature at various light intensities

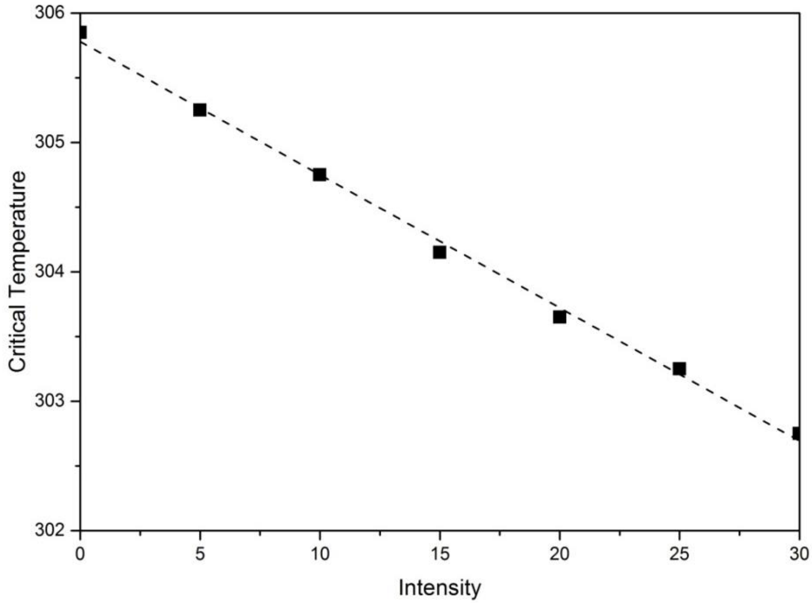
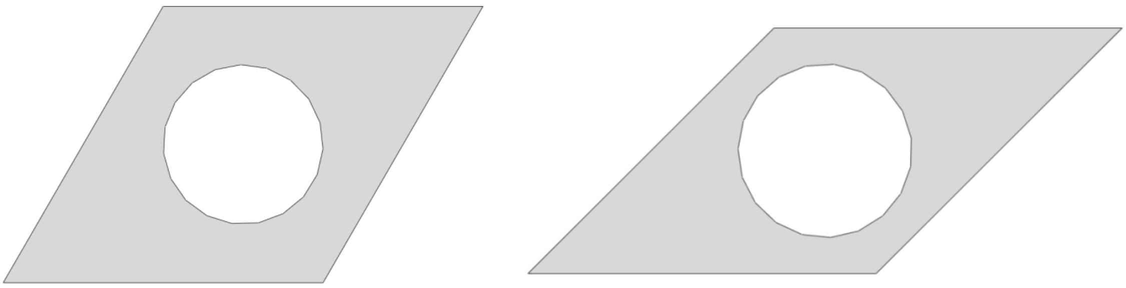


Fig. 7 Dependence of critical temperature of bifurcation on light intensity

3.1.2 Bifurcation of gel layer with staggered array of holes

In a square array of holes, bifurcation causes spontaneous transition into mutually perpendicular ellipses, which eventually close up into slits upon eventual swelling. This mutually perpendicular arrangement of slits, however, is dependent on the obliquity of the repeating unit. In addition to the square repeating unit, we now consider rhombic repeating units slanted at 60° and 45° to the horizontal, as shown in Fig. 8.

In initial simulations, unit cells of different configurations of repeating units ($m \times n$) were used and unfavourable results were obtained. This is due to the incorrect configuration of repeating units, thus rendering the simulations unable to obtain the periodic patterns. Eventually, 4×4 and 2×1 repeating units are required to form the unit cells for the cases of 60° and 45° obliquity respectively. These configurations were obtained by studying the pattern formation in finite sized unit cells of 10×10 repeating units, without any periodic boundary conditions applied.



(a) (b)

Fig. 8 Rhombic repeating unit slanted at (a) 60°, and (b) 45°

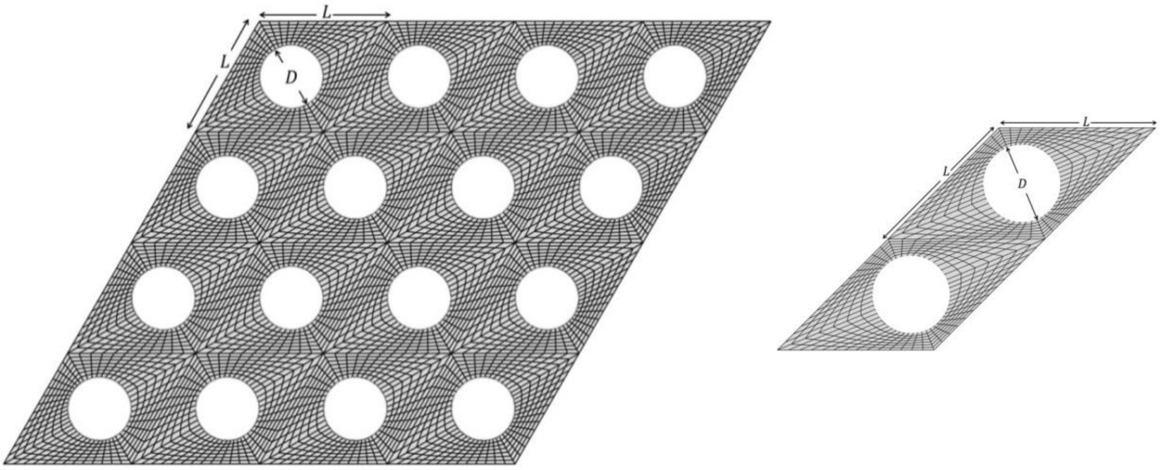


Fig. 9 Mesh of unit cell consisting of 4×4 and 2×1 repeating units for repeating units slanted at (a) 60° and (b). The lengths of each side of the repeating unit are 1.5 and diameters are 0.75

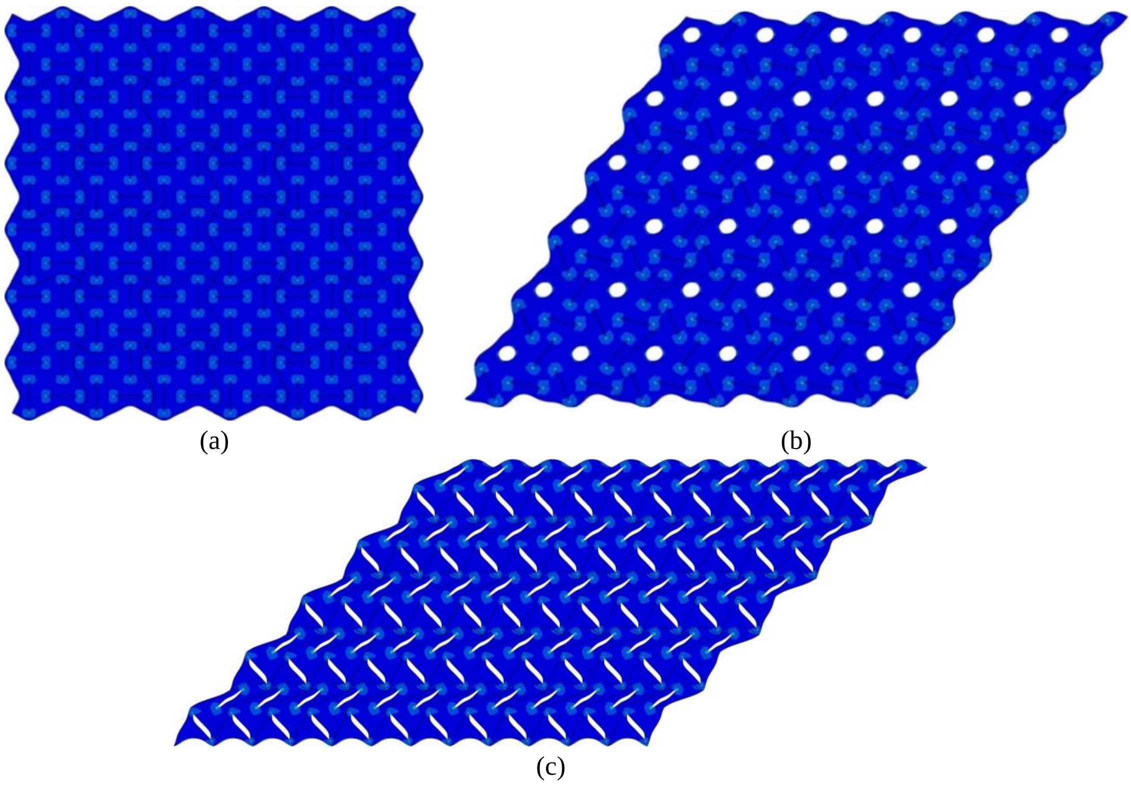


Fig. 10 Bifurcation pattern of gel layers with 12×12 repeating units for (a) square array, (b) rhombic array slanted at 60°, and (c) rhombic array slanted at 45°

Fig. 10 shows the deformed unit cell at 290 K for both obliquities. It is clearly seen that for different arrangements of the holes, we obtain different bifurcation patterns, and the size of openings after bifurcation are also different. This may be used as a design parameter for the control of end state sizes of pores required for different applications.

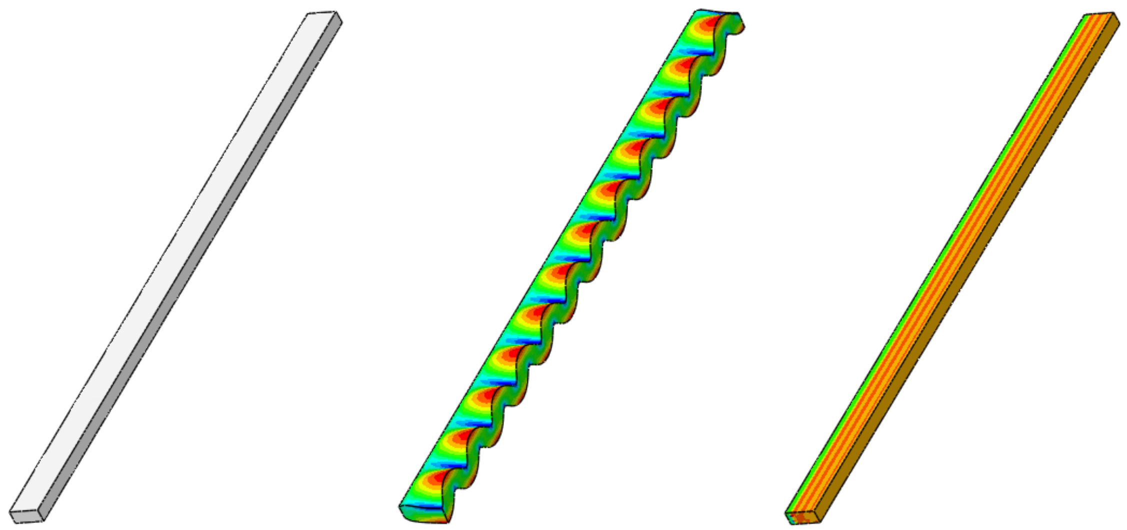
3.2 Buckling control of a gel strip

In the swelling of thin gel structures confined partially, compressive stresses build up and subsequently cause buckling of the gel structure into waves. Some geometries which exhibit the buckling of structures into these waves include a thin rectangular strip, a flat annulus and a thin walled ring (Lee *et al*. 2012, Mora and Boudaoud 2006). The size of the waves are hugely dependent on the geometry of the gel (Liu *et al*. 2010, Liu *et al*. 2011). For circular wavy structures, potential applications as soft gears have been proposed (Yin *et al*. 2009, Zhang *et al*. 2010).

In this section, we explore the buckling and unbuckling of a thin rectangular gel strip confined on one side laterally. It has been shown that the size of the buckled waves is related to the geometry. With a photo-thermal sensitive hydrogel, we note that the dependence on geometry remains, and it is not possible to alter the wave sizes through other forms of stimuli. However, it is possible to switch between the buckled state and the flat strip with application of light. As with the phase transition of a photo-thermal gel, the critical temperature of transition can be altered by changing light intensity.

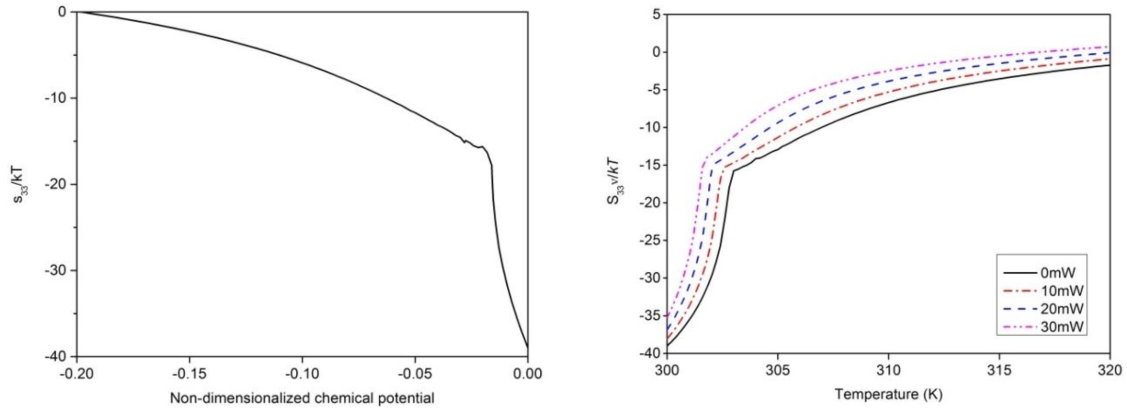
In this example, we investigate the effects of light intensity on the buckling and unbuckling of a gel strip of dimensions in the ratio t:B:L=1:2.5:100 (Fig. 11(a)). upon reaching equilibrium with the external solvent, the gel buckles into a wavy pattern (Fig. 11(b)), defined as the OFF state. Upon irradiation, the temperature increases and causes deswelling. Upon reaching the critical temperature, the waves disappear, returning into the flat geometry (Fig. 11(c)).

From the OFF state, it is possible to toggle to the ON state (flat geometry) and back with application of irradiation. Fig. 12(a) shows the maximum longitudinal stress present in the gel as it



(a) (b) (c)

Fig. 11(a) Initial geometry of gel in dry state, (b) gel in hydrated OFF state, (c) gel in irradiated ON state



(a) (b)

Fig. 12 Maximum longitudinal stress in gel as (a) dry gel is hydrated from $\bar{\mu} = -0.2$ to $\bar{\mu} = 0$, (b) buckled gel is irradiated with varying light intensities across a temperature range

is hydrated from $\bar{\mu} = -0.2$ to $\bar{\mu} = 0$. Fig. 12(b) shows the maximum longitudinal stress in the gel as it is being irradiated from the OFF state with different light intensities.

Due to the difference in light intensity, we see that for the same temperature rise in the gel, the critical transition where the buckled structure returns to a flat geometry is affected. This observation may be useful for active controlling purposes. As the buckled states can be toggled on and off by simply varying the light intensity.

4. Conclusions

The incorporation of light sensitive nanoparticles into temperature sensitive hydrogels is a viable option for remote controlled applications. In this paper, we have shown that the instabilities caused by hydration of a gel can be reversed by irradiation. With irradiation of different intensities, the transition between buckled and unbuckled modes can be precisely controlled. More specifically, the critical temperature at which unbuckling of the structure decreases as intensity of light is increased. This provides a useful property where structures can be made to transform from one shape to another, at precise temperatures which can be controlled by the intensity of irradiation. In addition, it has also been shown that in a gel layer with a periodic array of holes, the initial placement of perforations in the gel causes the bifurcation of the structure to result in different transformed patterns. This observation is useful in obtaining various geometries in applications such as micro-patterning.

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