Communication

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Constrained swelling and instability of a temperature-sensitive hydrogel ring

Abstract: We analyze the constrained swelling of a temperature-sensitive hydrogel ring, a key component of a previously developed adaptive liquid microlens. Hard constraints make the deformation and stress distribution within the gel nonuniform. The compressive stress may even cause the instability of the ring. We code a material model for poly(N-isopropylacrylamide) hydrogel and predict wrinkling instability at the inner periphery of the ring by using a commercial finite element method software. The presented model and the codes can be utilized to aid the design of soft devices based on temperature-sensitive hydrogels.

Keywords: finite element method; hydrogel; instability; swelling; temperature-sensitive.

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1 Introduction

Hydrogels are soft active materials that can adaptively deform in response to a variety of stimuli, including salt, pH, light, temperature and electric/magnetic fields. Stimuli-responsive hydrogels have been exploited to develop flow regulators, adaptive optics, swelling packers and soft robotics (1–5). Among the family of stimulus-responsive hydrogels, the temperature-sensitive hydrogel, poly(N-isopropylacrylamide) (PNIPAM) hydrogel, has attracted intense attention due to its unique features such as simplicity to synthesis, ease of tunability and good integrability. As a typical example, PNIPAM hydrogels have been utilized to construct adaptive microlenses (3, 6, 7).

The development of these hydrogel-based structures often involves hybrids of soft hydrogels and hard constraints. The constrained swelling of hydrogel would induce inhomogeneous stress distribution and large deformation responsible for numerous phenomena ranging from cavities, wrinkles and other intriguing instability patterns (8, 9).

2 Model and analysis

On the basis of the recently formulated field theories of constrained swelling of hydrogels (10–12), we analyze the inhomogeneous swelling of a temperature-sensitive hydrogel ring. It can be regarded as a model system for the analysis of adaptive liquid microlenses. The analytical model results in a boundary-value problem (BVP) of second-order ordinary differential equation (ODE), and we solve the BVP by using a shooting technique. To validate the BVP results and to further predict more complex deformation, we program a user material subroutine (UHYPER) for a commercial finite element method (FEM) software, ABAQUS (Dassault Systemes Simulia Corp., Providence, RI, USA). The UHYPER can capture the wrinkling instability of the temperature-sensitive hydrogel ring.

Figure 1 schematizes various states of a PNIPAM hydrogel ring for microlens application. The field variables of the theory are defined with respect to a reference dry state shown in Figure 1A, where the ring has inner and outer radii, A and B, respectively, and height H. The radial material coordinate of a representative point is R. We start from an initial stress-free state, where the ring swells isotropically in three principal directions by the same degree λ_0 at a formation temperature T_0. λ_0 also relates to the amount of water at formation (11). The hydrogel ring was then assembled to give a liquid microlens structure as shown in Figure 1B and C. The liquid lens uses the meniscus between the contained water and the surrounding oil as optical lens. Upon variation of temperature, the hydrogel ring swells and changes the curvature and thus the focal length of the lens. The material point deforms to current state with radial coordinate, r. The height and the outer periphery of the ring are constrained, and "slipping conditions" are adopted on the interfaces between the hydrogel and the base glass and top aperture in view of experimental realization; thus, the ring can only expand or contract at the inner periphery.
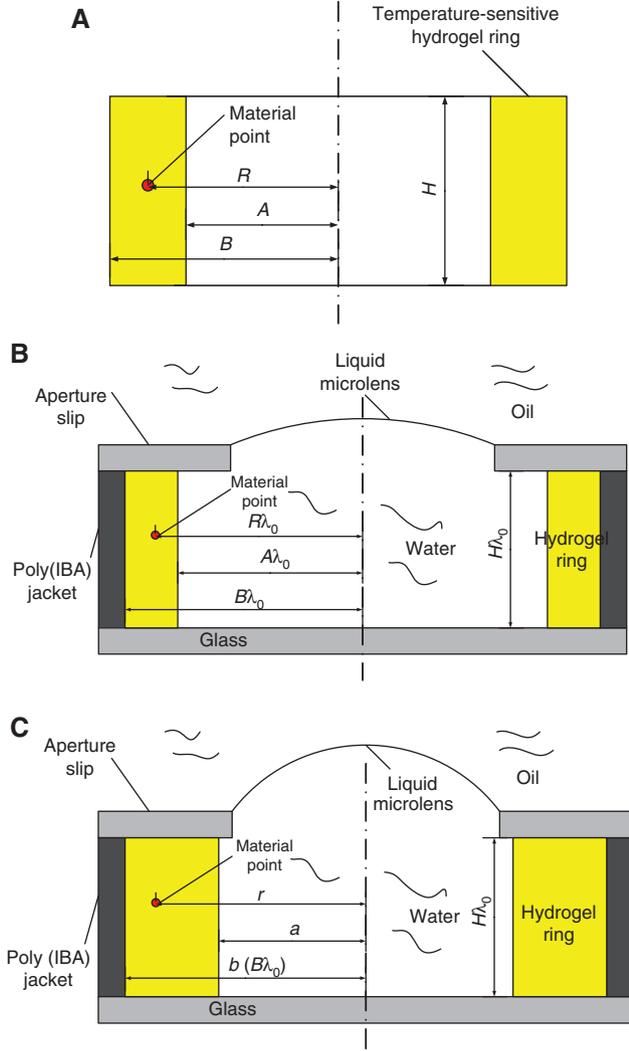
Figure 1 Schematic of various states of a temperature-sensitive hydrogel ring used for an adaptive liquid microlens. (A) Reference state of a dry polymer network with dimensions *A, B* and *H* and a material point with radial coordinate *R*. (B) Initial state of the hydrogel after an isotropic swelling λ_0. The hydrogel ring was then sandwiched between a glass plate and an aperture slip and placed around a polymer jacket. The contained water and the oil on top of the structure form an oil-water interface functioning as a liquid lens. (C) Changing temperature causes the swelling of the ring with inner and outer radii in current state *a* and *b*, respectively. The swelling of the ring finally induces the variation of the curvature of the meniscus and the focal length of the microlens.

The deformation of the ring is assumed to be axisymmetric, hence *r* is only a function of *R*, i.e., $r(R)$. The hoop stretch is defined as $\lambda_\theta = r/R$, and the radial stretch is defined as $\lambda_r = dr/dR$. Denoting *C* as the number of water molecules divided by the volume of dry polymer volume and *v* as the volume of a water molecule, the incompressibility conditions dictate $\lambda_r \lambda_\theta \lambda_z = 1 + vC$. The current height and the outer radius of the ring, *b*, were set to $\lambda_0 H$ and $\lambda_0 B$, respectively, due to the constraints.

Following Cai and Suo (13), the theory of gels starts from the expression of its free energy, which is expressed in terms of cylindrical coordinates as:

$$W(\lambda_r, \lambda_\theta, \lambda_z, T) = kT\left[C\log\frac{vC}{1+vC} + \frac{\chi C}{1+vC}\right]$$
$$+ \frac{1}{2}NkT\left[\lambda_r^2 + \lambda_\theta^2 + \lambda_z^2 - 3 - 2\log(\lambda_r\lambda_\theta\lambda_z)\right] \quad [1]$$

where *N* is the number of polymer chains per reference volume, *k* is Boltzmann constant and *T* is the absolute temperature. The first part of free-energy expression represents the free energy due to mixing of polymer network and solvent, while the second part gives the free energy due to stretching of the polymer network. For temperature-sensitive hydrogel, the Flory-Huggins parameter is a function of *T* and is defined as (13–15):

$$\chi(T, C) = \chi_0 + \chi_1\varphi = A_0 + B_0 T + (A_1 + B_1 T)/(1 + vC). \quad [2]$$

The coefficients A_i and B_i, are fitted to experiments of PNIPAM hydrogels and a lot of data were accumulated in the literature. With the expression of free energy of hydrogel, the nominal stresses are evaluated by taking the derivative of free energy with respect to individual stretch, which gives

$$\frac{s_i}{NkT} = \lambda_i - \lambda_i^{-1} + \frac{1}{Nv}\cdot\frac{1+vC}{\lambda_i}\cdot\left[\log\frac{vC}{1+vC} + \frac{1}{1+vC} + \frac{\chi_0 - \chi_1}{(1+vC)^2}\right.$$
$$\left. + \frac{2\chi_1}{(1+vC)^3}\right], \quad (i=r,\theta). \quad [3]$$

The stresses defined in Eq. [3] should satisfy the following equilibrium equation in cylindrical coordinates:

$$\frac{ds_r}{dR} + \frac{s_r - s_\theta}{R} = 0. \quad [4]$$

From Eq. [4] a second-order ODE about $r(R)$ can be deduced as follows:

$$r''\left[1 + \frac{1}{r'^2} - \frac{R}{Nv\cdot r'^2\cdot(R\cdot\lambda_0\cdot r\cdot r')} - \frac{2R}{Nv\cdot r^2\cdot r'^4}\left(\frac{(\chi_0 - \chi_1)\cdot r\cdot r'}{\lambda_0} + \frac{3R\cdot\chi_1}{\lambda_0^2}\right)\right]$$
$$- \frac{(r - R\cdot r')}{Nv\cdot r\cdot r'}\left[\frac{1}{\lambda_0\cdot r\cdot r' - R} - \frac{2(\chi_0 - \chi_1)}{\lambda_0\cdot r\cdot r'} - \frac{6R\cdot\chi_1}{\lambda_0^2\cdot r^2\cdot r'^2}\right] - \frac{1}{R\cdot r'} - \frac{r}{R^2} + \frac{r'}{R} + \frac{1}{r} = 0,$$

$$[5]$$

where prime denotes the derivative of *r* with respect to *R*. Eq. [5] is a nonlinear BVP and can be solved numerically by a shooting technique (16). The associated boundary conditions are $r(B) = \lambda_0 B$ and $s_r(A) = 0$. Fixing the chemical potential of the outside solution as zero and setting an arbitrarily initial swelling ratio, $\lambda_0 = 1.8$, the parameters used for all following calculations are $Nv = 0.01$, $B/A = 2$,

$A_0=-12.947$, $B_0=0.04496K^1$, $A_1=17.92$, $B_1=-0.0569K^1$ and $T_0=305.5$ K (13–17).

3 Results and discussion

Figure 2 plots the radial and hoop stretches by solving the BVP for various temperatures. The dashed line in Figure 2 represents the initial isotropic swelling ratio, λ_0, for both. Starting from this initial isotropic state, mechanical constraints make the following deformation inhomogeneous and the radial and hoop stretches do not equal any more: radial stretch increases above λ_0, but hoop stretch drops below λ_0 for a swelling process. Near the outer perimeter, λ_θ approaches λ_0 due to the constraints; λ_r approaches a plateau above λ_0 for a swelling case considered herein and vice versa for a shrinking case. In Figure 2, the radial coordinate is scaled by A.

Figure 3 plots the stresses for various temperatures. We note that both radial and hoop stresses are compressive. In Figure 3, stresses are normalized by the shear modulus of the network, NkT. Figure 3 indicates that the distribution of the radial and hoop stresses are different for such a constrained ring: the maximum compressive stress occurs at the inner periphery of the ring, whereas radial stress varies from zero to maximum value from the inner boundary to the outer boundary.

Another point of primary interest is the swelling volume ratio of the ring at various temperatures from 285 K to 305 K, which is plotted in Figure 4. The blank circles are discrete swelling ratios obtained by solving the BVP,
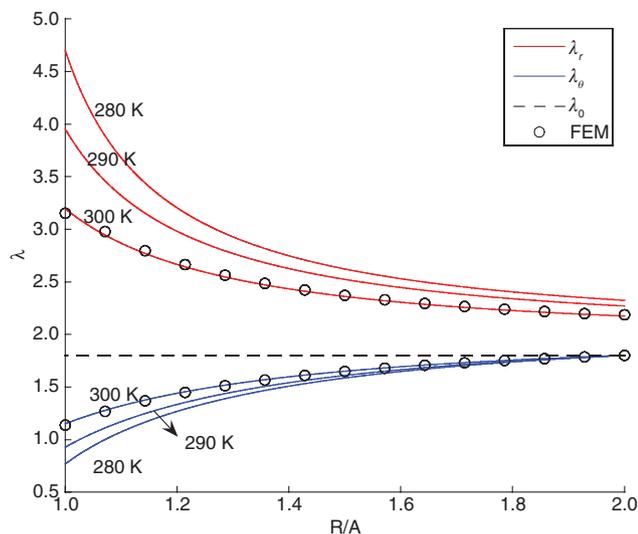

Figure 3 Radial and hoop stresses of a constrained hydrogel ring at various temperatures. The stresses were normalized by the shear modulus of the hydrogel, NkT. A comparison of FEM and BVP results was given for $T=300$ K.
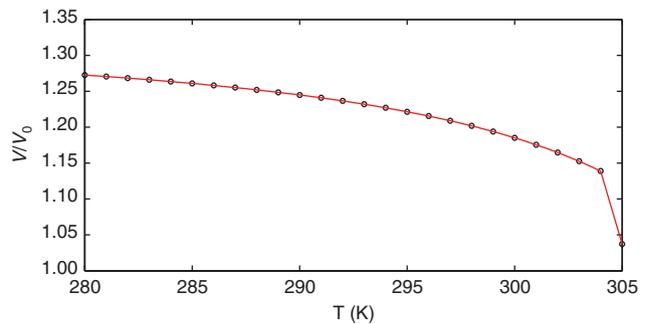
Figure 4 Swelling volume ratio of the hydrogel ring at various temperatures. Volume phase transition occurs near 305 K.

and the red solid line is the continuous curve that interconnects the circles. The swelling volume ratio is defined as V/V_o, where V and V_o are volumes of the hydrogel at current swollen state and the initial state, respectively. Notice that the swelling volume ratio drops abruptly at nearly 305 K, where a volume-phase transition occurs for such a temperature-sensitive gel.

The constrained swelling induces nonuniform distribution of deformation and stress within the gel. The magnitude as well as the tensile or compressive stress state is of great importance for such microscale devices. For this particular hydrogel ring configuration, the developed compressive stresses may cause instability. On the basis of a previously code developed by Hong et al. (17), we program a user-defined UHYPER subroutine for the PNIPAM hydrogel in a commercial finite element package, ABAQUS. With that, we can validate the BVP results and model wrinkling instability of the hydrogel ring. In Figures

Figure 2 Radial and hoop stretches vs. normalized radius of the hydrogel ring for various temperatures. The BVP and FEM results were compared for $T=300$ K.
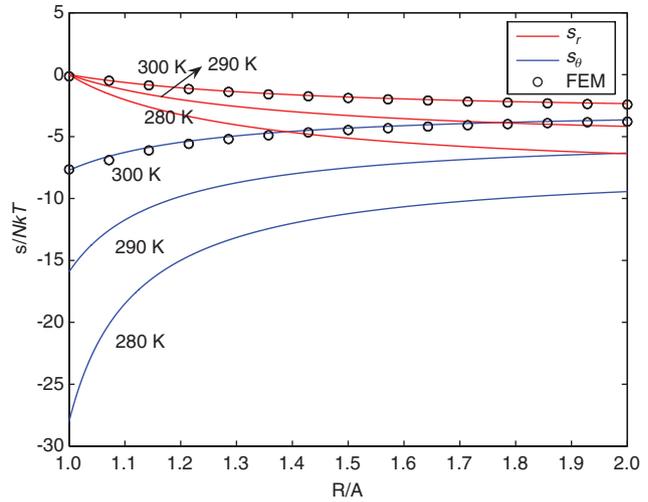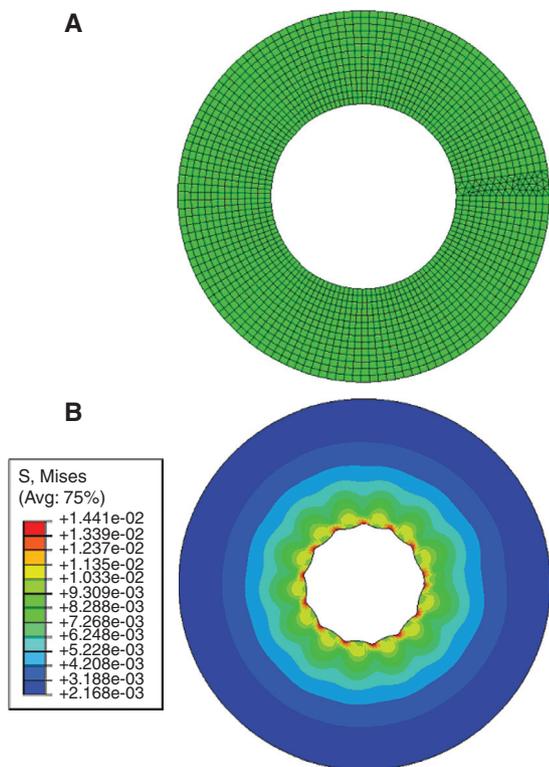
A

B

S, Mises
(Avg: 75%)

> +1.441e-02
> +1.339e-02
> +1.237e-02
> +1.135e-02
> +1.033e-02
> +9.309e-03
> +8.288e-03
> +7.268e-03
> +6.248e-03
> +5.228e-03
> +4.208e-03
> +3.188e-03
> +2.168e-03

Figure 5 The swelling induced wrinkles at the inner periphery of the hydrogel ring. (A) Initial state of the hydrogel ring at T=305.5 K. A localized irregular mesh was introduced to mimic the imperfection. (B) Swollen and wrinkled state of the ring at T=300 K. The stress is normalized by KT/v.

2 and 3, comparison of BVP and FEM results are shown for T=300 K with the FEM results marked by circles. Figure 5 shows the wrinkling instability of the inner periphery of the ring at T=300 K. To model such a wrinkling instability, one needs to introduce imperfection. Here the imperfection is introduced by a localized irregular mesh.

4 Concluding remarks

In summary, we present a model to analyze the constrained swelling of a temperature-sensitive hydrogel ring for adaptive microlens applications. We programmed a user-defined UHYPER subroutine for the PNIPAM hydrogel and integrated the code into a commercial FEM package. The model and the codes would aid the design of soft machines based on temperature-sensitive hydrogels. The model, however, is still rough and cannot correlate theoretical analysis to experiments of liquid microlenses. Modifications of the model to account for the difference of bound and free water molecules within the hydrogel are expected.

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