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Drying-induced cavitation in a constrained hydrogel

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Cavitation can be often observed in soft materials. Most previous studies were focused on cavitation in an elastomer, which is under different mechanical loadings. In this paper, we investigate cavitation in a constrained hydrogel induced by drying. Taking account of surface tension and chemo-mechanics of gels, we calculate the free energy of the system as a function of cavity size. The free energy landscape shows a double-well structure, analogous to first-order phase transition. Above the critical humidity, a cavity inside the gel is tiny. Below the critical humidity, the size of the cavity is large. At the critical humidity, the cavity size grows suddenly and discontinuously. We further show that local large stretches can be induced in the gel during the drying process, which may result in fractures.

Cavitation in an elastomer induced by internal pressure in the cavity or external tension on its outer boundary has been intensively studied both theoretically and experimentally.^{1–7} When the internal pressure or external tension exceeds a critical value, a sudden growth of an initially infinitesimal cavity has been observed in experiments and predicted by different theories.⁸ Such phenomenon has been recently successfully exploited to measure elasticity of soft materials.^{9,10} For most soft elastomers such as rubbers and many soft biological tissues, their shear moduli are several orders of magnitude lower than their bulk moduli, so the material is assumed to be incompressible in most previous studies.

However, hydrogel, as one widely observed and used soft material, can change volume dramatically by releasing or absorbing water. In particular, change of environmental humidity can induce large deformation in hydrogels. For instance, diverse deformation modes have been observed and predicted in the structures composed of gels during the drying

process.^{11–13} Expansion of the cavity in the hydrogel during the drying process has also been observed experimentally.¹⁴ However, the formulation of drying-induced cavity growth in a constrained hydrogel and the corresponding analyses are not available. In this communication, taking account of surface tension and chemo-mechanics of hydrogels, we study the cavitation in a constrained hydrogel in the drying process.

The problem we study in this communication is sketched in Fig. 1. A stress-free dry spherical gel with radius B and a tiny cavity with radius A is taken as the reference state (Fig. 1a). In this article A/B is set to be 0.02. The gel then swells freely in pure water with swelling ratio λ_0 (Fig. 1b). Using Flory–Rehner's free energy,^{15,16} the swelling ratio can be determined by the following equation,

$$N\Omega(\lambda_0^{-1} - \lambda_0^{-3}) + \log(1 - \lambda_0^{-3}) + \lambda_0^{-3} + \chi\lambda_0^{-6} = 0, \quad (1)$$

where N is the number of polymeric chains per reference volume, Ω is the volume per water molecule and χ is a dimensionless measure of mixing enthalpy.

The swollen gel is then constrained by a rigid but permeable wall on its external boundary. With the decrease of environmental humidity, the amount of water in the gel will reduce and the cavity grows as shown in Fig. 1c. In this investigation, we focus on the equilibrium state of gels, namely, the chemical potential of solvent in the gel is the same as the chemical potential of solvent in the environment. Transient evolution of cavity size and the distribution of solvent concentration in the gel are beyond the scope of the communication.

In the drying process, the deformation in the gel is spherically symmetric. In the reference state, an infinitesimal element of the network is defined by its distance R from the center. In the equilibrium state, the same element moves to a new position at the distance r from the center. Considering the spherically symmetric deformation, the radial and hoop stretches can be calculated as

$$\lambda_r = \frac{dr}{dR}, \quad \lambda_\theta = \frac{r}{R}. \quad (2)$$

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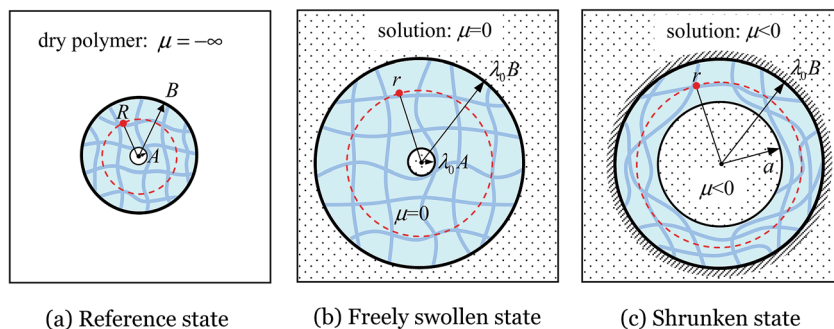


Fig. 1 (a) Dry spherical polymer network with a small cavity inside, which is taken as the reference state in the article. (b) Free swollen state of the polymer network. (c) With constraint boundary, the cavity grows with decreasing chemical potential of water (or environmental humidity). We assume that the deformation in the gel is elastic in the drying process.

Following previous studies on hydrogels,¹⁵ we assume both polymeric network and water molecules are incompressible, namely,

$$\lambda_r \lambda_\theta^2 = 1 + \Omega C. \quad (3)$$

where C is the number of water molecules in the hydrogel divided by the volume of the dry network.

Let s_r and s_θ be the nominal stresses in radial and hoop directions, respectively. Using the Lagrangian coordinates, the force balance in the radial direction is

$$\frac{ds_r}{dR} + 2 \frac{s_r - s_\theta}{R} = 0. \quad (4)$$

Using the free energy of Flory and Rehner,^{15,16} the state equations of the spherical hydrogel can be written as

$$\frac{s_r}{NkT} = \frac{\lambda_r^2 - 1}{\lambda_r} + \frac{\lambda_\theta^2}{N\Omega} \left[\log \left(1 - \frac{1}{\lambda_r \lambda_\theta^2} \right) + \frac{1}{\lambda_r \lambda_\theta^2} + \frac{\chi}{\lambda_r^2 \lambda_\theta^4} - \frac{\mu}{kT} \right], \quad (5)$$

$$\frac{s_\theta}{NkT} = \frac{\lambda_\theta^2 - 1}{\lambda_\theta} + \frac{\lambda_r \lambda_\theta}{N\Omega} \left[\log \left(1 - \frac{1}{\lambda_r \lambda_\theta^2} \right) + \frac{1}{\lambda_r \lambda_\theta^2} + \frac{\chi}{\lambda_r^2 \lambda_\theta^4} - \frac{\mu}{kT} \right], \quad (6)$$

where μ is the chemical potential of water molecules in the gel, which is equal to the chemical potential of water in the environment. Therefore, the chemical potential can be related to the relative humidity by $\mu = kT \log \text{RH}$, where RH is the relative humidity in the environment. The chemical potential of water is zero for 100% relative humidity. When the relative humidity is smaller than 100%, the chemical potential of water is negative.

A combination of eqn (2)–(6) gives the governing equations of $r(R)$. The boundary condition for the outer boundary is $r(B) = \lambda_0 B$. With prescribing the cavity size $r(A)$, the field $r(R)$ can be calculated. We can subsequently calculate the deformation field, namely, $\lambda_r(R)$ and $\lambda_\theta(R)$.

Next, we calculate the free energy of the gel with different sizes of cavities. Following Flory–Rehner's model,^{15,16} the free energy density of a gel undergoing homogeneous deformation

can be decomposed into the elastic energy of a stretching polymer network and free energy of mixing between the solvent and polymer:

$$w_s = \frac{1}{2} NkT [\lambda_r^2 + 2\lambda_\theta^2 - 3 - 2 \log(\lambda_r \lambda_\theta^2)], \quad (7)$$

$$w_m = -\frac{kT}{\Omega} \left[\Omega C \log \left(1 + \frac{1}{\Omega C} \right) + \frac{\chi}{1 + \Omega C} \right]. \quad (8)$$

In this study, we take account of the effects of surface tension of the cavity surface. The deformation of the gel is inhomogeneous, so the free energy of the gel can be obtained by the following integration,

$$F = \int_V (w_s + w_m - \mu C) dV + 4\pi [r(A)]^2 \gamma, \quad (9)$$

where γ is the surface energy per unit area of the cavity in the hydrogel.

Fig. 2 plots the free energy of the spherical gel as a function of its cavity size for different chemical potential of water (or environmental humidities). For a certain range of chemical potential, the free energy landscape shows a double-well

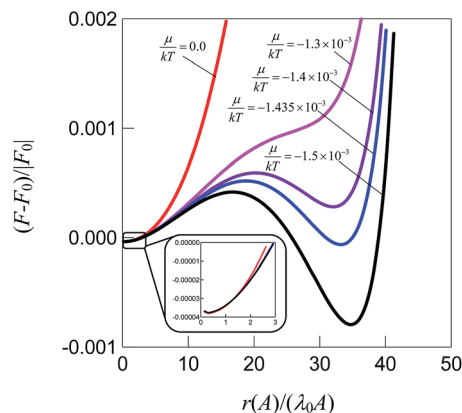


Fig. 2 The free energy landscape of a constrained spherical gel with a cavity at different chemical potential of water (or different environmental humidities). In the figure, the surface energy density is $\gamma / (NkTA) = 20$. F_0 is the free energy of a spherical gel without cavity.

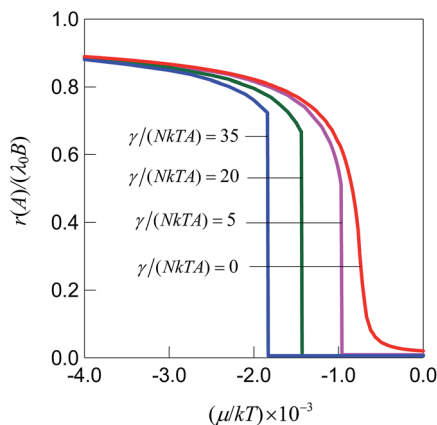


Fig. 3 The size of the cavity as a function of chemical potential of water in the environment with different surface energy densities. When the surface energy density is nonzero, a discontinuous jump of the cavity size is predicted by the theory.

structure, analogous to first-order phase transition. At a critical chemical potential (or critical humidity), two energy minima, corresponding to small and large cavities, have equal value. The cavity jumps from a small one to a large one discontinuously. In the calculation, the material parameters are set to be $N\Omega = 10^{-3}$ and $\chi = 0.2$, which are typical parameters for a hydrogel. We would also like to note that similar to the classical

cavitation problem in elastomers, the initial cavity size introduced into the gel is infinitesimal compared to the size of the gel ($A/B = 0.02$).

By selecting the cavity size which minimizes the total free energy of the gel, the radius of the cavity is plotted as a function of chemical potential of water in Fig. 3 for several different surface energy densities. When the chemical potential of water (or environmental humidity) is large, the cavity is small. When the chemical potential of water is smaller than a critical value, the radius of cavity increases discontinuously. It also shows that the critical chemical potential of water is lower for larger surface tension. In particular, when the surface energy density is zero, the growth of the cavity becomes continuous.

In this study, we assume that the growth of the cavity is elastic and possible plastic deformation or even fractures are ignored in the analysis. In Fig. 4, we plot both radial stretch field and hoop stretch field for several different chemical potential of water. In reality, when the stretch or stress exceeds the strength of gels, fracture can happen and the subsequent growth of a cavity will be dominated by crack propagation which is beyond the scope of this article.

In summary, we study the cavitation instability of a gel in the drying process with constraint. Taking account of surface energy of the cavity and chemo-mechanics of the gel, a sudden and discontinuous growth of the cavity is predicted by our models, which is analogous to first-order phase transition. We expect that experimental validations of our models will be available in the future.

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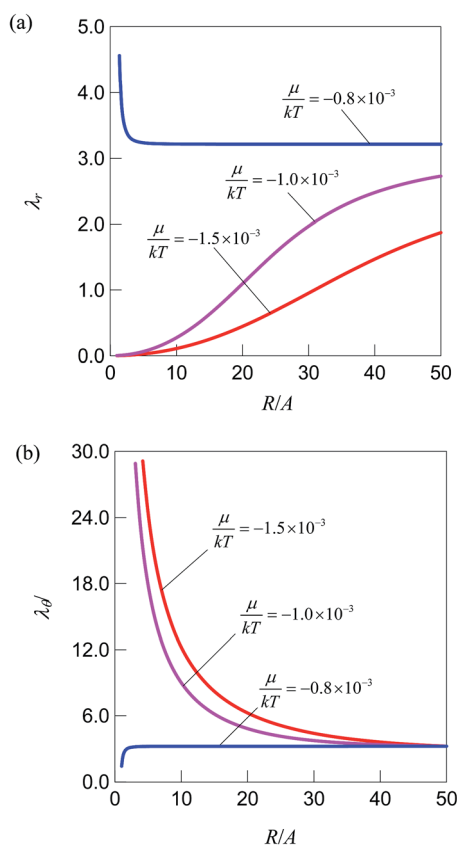


Fig. 4 The distribution of (a) radial and (b) hoop stretch for different chemical potential of water with surface energy density $\gamma/(NkTA) = 5$.

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