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Drying-induced bifurcation in a hydrogel-actuated nanostructure

Wei Hong,^{a)} Xuanhe Zhao, and Zhigang Suo^{b)}

School of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts 02138, USA

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Hydrogels have enormous potential for making adaptive structures in response to diverse stimuli. In a structure demonstrated recently, for example, nanoscale rods of silicon were embedded vertically in a swollen hydrogel, and the rods tilted by a large angle in response to a drying environment [Sidorenko *et al.*, *Science* **315**, 487 (2007)]. Here we describe a model to show that this behavior corresponds to a bifurcation at a critical humidity, analogous to a phase transition of the second kind. The structure adapts to the drying environment in two ways. Above the critical humidity, the rods stand vertical, enabling the hydrogel to develop tension and retain water. Below the critical humidity, the rods tilt, enabling the hydrogel to reduce thickness and release water. We further show that the critical humidity can be tuned. © 2008 American Institute of Physics. [DOI: 10.1063/1.2996318]

I. INTRODUCTION

A hydrogel is an aggregate of a polymer network and mobile water molecules. In a humid environment, the hydrogel can swell by imbibing a large quantity of water. Swelling can also be induced by other stimuli, such as light, temperature, concentration of ions, and presence of enzymes.¹⁻³ Consequently, hydrogels have enormous potential for making adaptive structures (e.g., valves,⁴ lenses,⁵ and switches⁶) in response to diverse stimuli. These structures are typically miniaturized, alleviating a major limitation of actuation by hydrogels: the speed. Swelling rate of a hydrogel is limited by diffusion of water so that a small size leads to a fast response. Response time of some milliseconds has been demonstrated.⁶

The development of hydrogel-actuated structures has also led to another major consideration. A hydrogel is often integrated with hard materials, leading to a hybrid structure of soft and hard materials. Mechanical constraint in the hybrid structure can markedly affect the swelling behavior of the hydrogel, leading to inhomogeneous and anisotropic deformation.⁷⁻¹⁰ Yet few analyses exist to account for such complex deformation, possibly due to difficulties associated with nonlinearities. In this paper, we describe a model for a structure demonstrated recently,⁶ where mechanical constraint and nonlinearity are essential to the actuation of the structure.

Figure 1 illustrates the principle of actuation.⁶ Nanoscale rods of silicon are embedded in a hydrogel, which is bonded to a substrate of glass. When the hydrogel is swollen, the rods stand vertical [Fig. 1(b)]. As the environment dries, the hydrogel shrinks and tilts the rods [Fig. 1(c)]. The process is reversible. When the environment becomes humid, the hydrogel swells again, bringing the rods back to the vertical position. This adaptive structure may have a variety of applications including guided pattern formation, switching of

the wetting behavior, and tunable photonic structures. Here we describe a model to show that the adaptive behavior of the structure corresponds to a bifurcation at a critical humidity, and that the critical humidity can be tuned.

II. MODEL OF THE BIFURCATION

The hydrogel is bonded to the rods of silicon and to the substrate of glass. Both silicon and glass are much harder than the hydrogel and are taken to be rigid. The system has three lengths: the diameter of each rod, the length of each

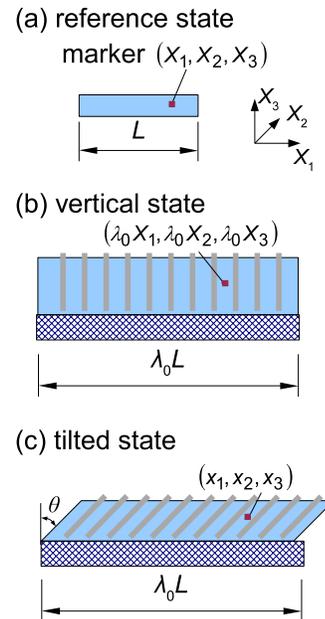


FIG. 1. (Color online) Principle of operation of a hydrogel-actuated nanostructure. Rigid rods are embedded in a hydrogel, which is bonded on a rigid substrate. (a) In the reference state, the polymeric network is water-free and stress-free. (b) In the vertical state, water in the hydrogel expands the network by an isotropic stretch λ_0 , and the rods stand vertical. (c) In the tilted state, the rods rotate by an angle θ . A marker attached to the network has the coordinates (x_1, x_2, x_3) in the reference state, has the coordinates $(\lambda_0 x_1, \lambda_0 x_2, \lambda_0 x_3)$ in the vertical state, and moves to (x_1, x_2, x_3) in the tilted state.

^{a)}Present address: Department of Aerospace Engineering, Iowa State University, Ames, IA 50011.

^{b)}Electronic mail: suo@seas.harvard.edu.

rod, and the spacing between neighboring rods. For the structure to be an effective switch, the rods must constrain the deformation of the gel; that is, the length of the rods should be much larger than the diameter of the rods and the spacing between the rods. Within a thickness comparable to the length of the rods, the deformation of the hydrogel is essentially homogeneous, as dictated by the rotation of the rigid rods. The rotation of the rods, however, is negligibly affected by the inhomogeneous deformation in the hydrogel on the top surface and near the bottom of the rods. To account for the full inhomogeneous deformation in the gel would require the solution of a detailed boundary value problem. The result would be unlikely to alter the basic picture of the bifurcation. In this paper, we will assume that the deformation in the gel is homogeneous.

The bifurcation is qualitatively understood as follows. If the rods remain vertical, the rods and the substrate will prevent the hydrogel from deforming in any direction, enabling the hydrogel to develop a state of isotropic tension and retain water. When the tension in the hydrogel becomes too high, however, the vertical rods become unstable and will tilt, enabling the hydrogel to reduce thickness and release water. The tilt of the rods breaks the symmetry of the structure. Consequently, we expect that the switching between the two states is analogous to a phase transition of the second kind.¹¹

We next turn this qualitative picture into a model. Large deformation in hydrogels can be analyzed using nonlinear field theories.^{12–16} Here we will follow the notation of our recent paper¹⁶ and adopt the free-energy function of gels developed by Flory and Rehner.¹⁷ This free-energy function has been critiqued by many authors, see Refs. 18 and 19 for reviews. The critiques, however, do not affect the essence of our model and will not be pursued here.

We take the dry network as the reference state, where the network is water-free and stress-free [Fig. 1(a)]. This reference state, however, need not be the state in which the structure is fabricated. For example, an aqueous solution of monomers may be introduced into the space between the rods and is then polymerized to form a layer of swollen hydrogel [Fig. 1(b)]. See Ref. 6 for the method of fabrication.

When the rods stand vertical, as discussed above, the hydrogel is constrained in all three directions and cannot deform. Instead, the hydrogel develops a state of isotropic tensile stress to counteract the drying environment. Using the equations of state of gels,¹⁶ which was derived from the free energy of Flory and Rehner,¹⁷ we obtain the magnitude of this stress

$$s = (\mu_0 - \mu)\lambda_0^2/v \quad (1)$$

with

$$\mu_0 = vNkT(\lambda_0^{-1} - \lambda_0^{-3}) + kT \left[\log \frac{\lambda_0^3 - 1}{\lambda_0^3} + \frac{1}{\lambda_0^3} + \frac{\chi}{\lambda_0^6} \right], \quad (2)$$

where λ_0 is the isotropic stretch of the network in the vertical state relative to the reference state, μ is the chemical potential of water molecules in the environment, v is the volume per water molecule, kT is the temperature in the unit of energy, N is the number of polymeric chains per reference vol-

ume, and χ is a dimensionless measure of the enthalpy of mixing. When $\chi > 0$, the enthalpy of mixing motivates water molecules to leave the hydrogel. Equation (2) gives the special value of the chemical potential μ_0 that makes the vertical state stress-free. When the chemical potential in the environment μ deviates from μ_0 , Eq. (1) gives the nominal stress s acting on the hydrogel in all directions. When the rods stand vertical, it is this stress that enables the hydrogel to adapt to the drying environment and retain water.

We next consider the tilt of the rods. Let X_1 and X_2 be the two axes in the layer of the hydrogel and X_3 be the axis normal to the layer. Without losing generality, we assume that the rods tilt by an angle θ around the X_2 axis. Imagine that we attach to an element of the polymeric network a marker, whose coordinates are (X_1, X_2, X_3) in the reference state and are $(\lambda_0 X_1, \lambda_0 X_2, \lambda_0 X_3)$ in the vertical state. When the rods tilt, the marker moves to a new position with the coordinates

$$x_1 = \lambda_0(X_1 + X_3 \sin \theta), \quad x_2 = \lambda_0 X_2, \quad x_3 = \lambda_0 X_3 \cos \theta. \quad (3)$$

The functions $x_i(X_1, X_2, X_3)$ describe the field of deformation in the hydrogel in the tilted state.

By definition, the deformation gradient \mathbf{F} has the components $F_{iK} = \partial x_i(X_1, X_2, X_3) / \partial X_K$. The deformation field (3) gives the deformation gradient tensor

$$\mathbf{F} = \begin{bmatrix} \lambda_0 & 0 & \lambda_0 \sin \theta \\ 0 & \lambda_0 & 0 \\ 0 & 0 & \lambda_0 \cos \theta \end{bmatrix}. \quad (4)$$

The volume of the hydrogel in the tilted state divided by the volume of the dry network is

$$\det(\mathbf{F}) = \lambda_0^3 \cos \theta. \quad (5)$$

This equation is readily understood. The substrate constrains the in-plane dimensions of the hydrogel so that the area of the hydrogel in the tilted state is λ_0^2 times the area in the reference state. The thickness of the hydrogel in the tilted state is $\lambda_0 \cos \theta$ times the thickness in the reference state. Equation (5) shows that the tilt causes the hydrogel to shrink in volume relative to the vertical state and allows the hydrogel to release water.

We assume that individual polymers and water molecules are incompressible so that the change in the volume of the hydrogel equals the volume of water imbibed, namely,

$$vC = \det(\mathbf{F}) - 1, \quad (6)$$

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

The hydrogel and the environment together constitute a thermodynamic system. We assume that the structure is immersed in a large environment in which water molecules move fast. Consequently, the chemical potential μ of water molecules in the environment remains constant as the polymer network imbibes or releases water. When the network imbibes a number of water molecules C , the free energy of the environment reduces by μC . Following Flory and Rehner,¹⁷ we assume that the free energy of the hydrogel

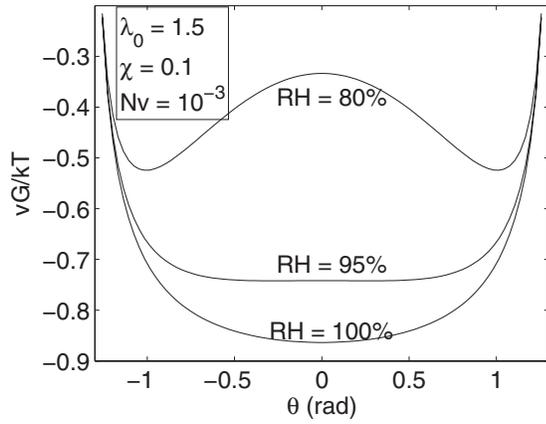


FIG. 2. The normalized free energy of the system vG/kT as a function of the angle of tilt θ . A critical humidity exists. When the environment is above the critical humidity, the free energy of the system has a single well at $\theta = 0$, and the rods stand vertical. When the environment is below the critical humidity, the free energy of the system has double wells, and the rods tilt.

consists of two contributions: stretching the polymer network and mixing the polymers with water molecules. The free energy of the composite system of the hydrogel and the environment is

$$G = W_s + W_m - \mu C \quad (7)$$

with the free energy due to stretching of the network being

$$W_s = \frac{1}{2} NkT [F_{iK} F_{iK} - 3 - 2 \log(\det \mathbf{F})] \quad (8)$$

and the free energy due to mixing the polymers and water molecules being

$$W_m = -\frac{kT}{v} \left[vC \log \left(1 + \frac{1}{vC} \right) + \frac{\chi}{1 + vC} \right]. \quad (9)$$

The free energy G reaches a minimum when water molecules in the hydrogel equilibrate with those in the environment.

A combination of the above equations gives the free energy of the system

$$\begin{aligned} \frac{vG(\theta)}{kT} &= \frac{1}{2} Nv [3(\lambda_0^2 - 1) - 2 \log(\lambda_0^3 \cos \theta)] \\ &+ (\lambda_0^3 \cos \theta - 1) \left(\log \frac{\lambda_0^3 \cos \theta - 1}{\lambda_0^3 \cos \theta} - \frac{\mu}{kT} \right) \\ &- \frac{\chi}{\lambda_0^3 \cos \theta}. \end{aligned} \quad (10)$$

The system has one degree of freedom, the angle of tilt θ , which directly relates to the amount of water in the hydrogel, [Eq. (6)]. The system has several control parameters: Nv , χ , λ_0 , and μ/kT . The chemical potential of water molecules in the saturated vapor is taken to be zero. The chemical potential of water molecules in an unsaturated environment relates to the relative humidity as $\mu = kT \log RH$. Figure 2 plots the function $G(\theta)$ at several levels of relative humidity. The behavior of the free energy switches at a critical humidity. When the environment is more humid than the critical humidity, the free energy has a single well at $\theta = 0$, and the rods stand vertical. When the environment is less humid than the

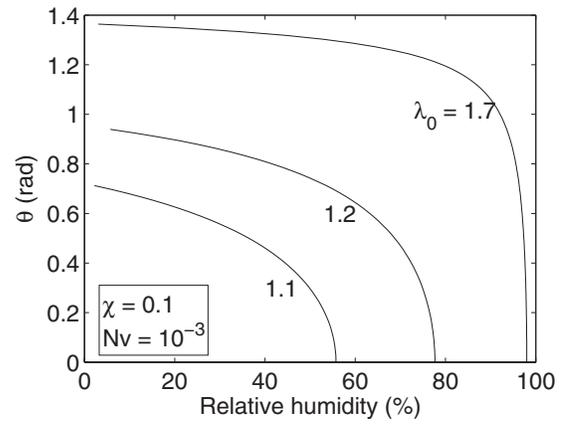


FIG. 3. The angle of tilt θ as a function of the relative humidity of the environment. The critical humidity can be varied by choosing the initial stretch λ_0 .

critical humidity, the free energy has double wells, and the rods tilt. Consequently, the tilt of the rods is a bifurcation analogous to a phase transition of the second kind.¹¹ The speed of the transition is set by the rate at which water molecules migrate in the gel and evaporate into the environment. This paper focuses on the energetics of the transition and will not discuss the kinetics of the transition.

Setting $dG/d\theta = 0$, we obtain both the equilibrium equation of the vertical state $\theta = 0$ and the equilibrium equation of the tilted state

$$\frac{\mu}{kT} = \frac{1 - Nv}{\lambda_0^3 \cos \theta} + \log \frac{\lambda_0^3 \cos \theta - 1}{\lambda_0^3 \cos \theta} + \frac{\chi}{(\lambda_0^3 \cos \theta)^2}. \quad (11)$$

Equation (11) gives the equilibrium angle of tilt when the environment is below the critical humidity. This equation is plotted in Fig. 3. For a given set of parameters, say $\lambda_0 = 1.2$, $\chi = 0.1$, and $Nv = 10^{-3}$, the rods stand vertical (i.e., $\theta = 0$) when the humidity in the environment is above a critical humidity ($RH_c \approx 78\%$ for this set of parameters), but the rods tilt by a large angle when the humidity in the environment drops slightly below the critical humidity. That is, near the critical point, the structure behaves like a switch, as expected from a bifurcation.

The critical humidity can be tuned. For example, Fig. 3 shows that the critical humidity varies with λ_0 , the stretch of the swollen hydrogel relative to the dry network. Besides λ_0 , the other two parameters, Nv and χ , can also affect the critical humidity. The critical chemical potential μ_c is obtained by setting $\theta = 0$ in Eq. (11) so that

$$\frac{\mu_c}{kT} = \frac{1 - Nv}{\lambda_0^3} + \log \frac{\lambda_0^3 - 1}{\lambda_0^3} + \frac{\chi}{\lambda_0^6}. \quad (12)$$

The parameter Nv is a dimensionless measure of the degree of cross links and is typically in the range of 10^{-5} – 10^{-2} . Equation (12) shows that a change in Nv has negligible effect on the critical humidity. The parameter χ is a dimensionless measure of the enthalpy of mixing the polymers and water molecules and is typically in the range of 0–1.2. Equation (12) shows that a change in χ , by using a polymer network of a different degree of hydrophobicity, can affect the critical humidity.

A combination of Eqs. (2) and (12) gives $(\mu_0 - \mu_c)/kT = Nv/\lambda_0$. Because $Nv \ll 1$, the critical humidity is close to the humidity that makes the vertical state stress-free. At the critical state, however, the tensile stress in the hydrogel can be substantial. Using Eq. (1), we obtain the tensile stress in the hydrogel in the critical state $s_c = NkT\lambda_0$, which scales with the elastic modulus of the dry network.

The expression of the free energy [Eq. (10)] is better understood by using a standard procedure for analyzing phase transitions of the second kind.¹¹ We expand the free energy [Eq. (10)] into the leading terms of a power series of the angle of tilt θ , namely,

$$G(\theta) = G(0) + \alpha(\mu - \mu_c)\theta^2 + \beta\theta^4, \quad (13)$$

where α and β are positive constants and μ_c is the critical chemical potential given by Eq. (12). The structure is symmetric when the rods stand vertical ($\theta=0$) so that the power series only contains even powers of θ . When $\mu > \mu_c$, the coefficient of θ^2 is positive, and the state $\theta=0$ minimizes the free energy. When $\mu < \mu_c$, the coefficient of θ^2 is negative, the state $\theta=0$ is a local maximum of the free energy, and the function minimizes at

$$\theta = A \left(\frac{\mu_c - \mu}{kT} \right)^{1/2} \quad (14)$$

with

$$A = \sqrt{\frac{2\lambda_0^3}{\frac{1}{\lambda_0^3 - 1} + Nv - \frac{2\chi}{\lambda_0^3}}}. \quad (15)$$

The parabolic behavior in Eq. (14) is generic to phase transitions of the second kind and shows once again that the rods tilt by a large angle when the humidity in the environment drops slightly below the critical humidity. Equation (15) shows that the angle of tilt is also affected by various parameters; for example, the variation with λ_0 is seen in Fig. 3.

III. CONCLUDING REMARKS

This adaptive structure illustrates a promising design strategy. The response of hydrogels to various stimuli, while impressive, can be greatly enriched by integrating with other materials in hybrid structures. The hybrid structures can amplify the response and tune the position of the critical point. For the hydrogel described in our model, for example, the amount of swelling of a stand-alone hydrogel varies gradually in the whole range of humidity, except near 100% relative humidity. Consequently, the swelling of the stand-alone hydrogel is not a sensitive indicator of the humidity. By con-

trast, the behavior of the hybrid structure changes drastically at a critical humidity, and the critical humidity can be tuned to a desired position well below 100% relative humidity. The strategy of hybrid structures complements that of designing molecular architectures for new hydrogels.¹⁻³ The interplay of the two strategies is also a rich area of future research.

In summary, the hybrid structure of a hydrogel and an array of rigid rods adapts to a drying environment in two ways, switching at a critical humidity. Above the critical humidity, the rods stand vertical, enabling the hydrogel to develop stress and retain water. Below the critical humidity, the rods tilt, enabling the hydrogel to shrink and release water. The critical humidity can be tuned by the water content in the swollen hydrogel and by the degree of hydrophobicity of the polymer network. Our model can be readily modified for hydrogels responsive to stimuli other than humidity. The model shows that the behavior of a hydrogel can be greatly enriched by integrating with hard materials. It will be fascinating to exploit the versatility of hydrogels to design other hybrid structures with unusual and useful properties.

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