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Creases and wrinkles on the surface of a swollen gel

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Consider a layer of a gel attached to a rigid substrate, immersed in a solvent, and swelling in the thickness direction. The flat surface of the gel remains stable if the swelling ratio is small, but becomes unstable if the swelling ratio is large. While creases have been commonly observed, wrinkles have also been observed under certain conditions. We compare the critical conditions for the onset of creases and wrinkles by using a nonlinear field theory of gels. The critical swelling ratio for the onset of creases is calculated by using a finite element method, and that for wrinkles is calculated by using an analytical method. We find that the critical swelling ratio for the onset of creases is significantly lower than that for wrinkles. © *2013 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4818943]

I. INTRODUCTION

Long and flexible polymer chains can be covalently crosslinked to form a three-dimensional network, an elastomer. When the network absorbs a solvent, the aggregate is known as an elastomeric gel. Associated with the absorption of the solvent, the network may swell many times the volume of the dry polymer. Swelling is usually under constraint, often leading to instability. For example, as a gel absorbs water, the surface swells more than the interior, resulting in instability (Fig. 1). As water migrates in further, the surface pattern coarsens and eventually disappears. Instability also occurs readily when a gel is subject to an applied force (Fig. 2). For a starch gel prepared in a tray, a stiff skin layer forms on the top surface of the gel due to the evaporation of water. When the gel is bent to compress the top surface, multiple wrinkles form. By contrast, when the same gel is bent to compress the bottom surface (without a skin layer), a single crease forms. For a gel attached to a rigid substrate and swelling in the thickness direction, the surface of the gel remains flat when the swelling ratio is small, but forms creases when the swelling ratio is large.[1–6]

Here, we compare the critical conditions for the onset of creases and wrinkles by using a nonlinear field theory of elastomeric gels. Both creases and wrinkles set in by deviating from a state of homogenous deformation (Fig. 3). Wrinkles deviate from the homogenous state by a field of strain infinitesimal in amplitude, but finite in space. Creases deviate from the homogenous state by a field of strain large in amplitude, but infinitesimal in space.[7] We analyze the onset of wrinkles by using an analytical method, and analyze the onset of creases by using finite-element methods. We find that the critical swelling ratio for the onset of creases is significantly lower than that for wrinkles. This theoretical finding is consistent with experimental observations. While creases are readily observed during swelling, we are unaware of any experimental evidence of wrinkles localized on the surface during swelling, except for incidences in which the gel has thickness-graded properties.

This paper is organized as follows. Section II summarizes the nonlinear field theory of elastomeric gels. An analytical method is presented in Sec. III to predict the critical condition for the onset of wrinkles. In Sec. IV, the inhomogeneous deformation of the gel in the creased state is calculated by the finite element method, and the critical condition for the onset of creases is determined. The critical conditions for wrinkles and creases are compared and discussed in Sec. V, followed by concluding remarks in Sec. VI.

II. A NONLINEAR FIELD THEORY OF GELS

Here, we summarize the nonlinear field theory of elastomeric gels.[8] A gel is a polymer network swollen with a

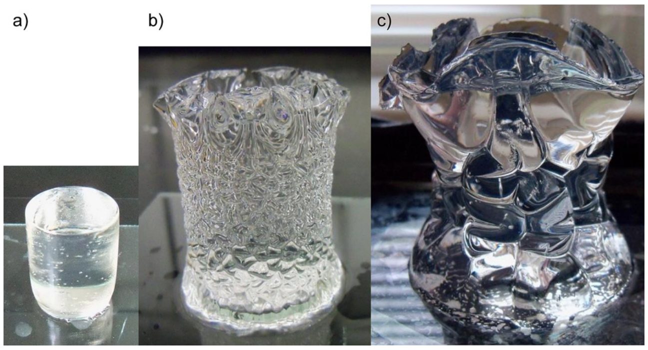

FIG. 1. Swelling-induced instability in a gel. The gel was synthesized using dimethylaminoethylmethacrylate and acrylamide as monomers, N,N′-methylenebisacrylamide as crosslinkers, and ammonium persulfate as initiators. (a) The as-fabricated gel, diameter ~3 cm. (b) During swelling in water, the surface of the gel formed creases. (c) As the migration of water progressed, the surface pattern coarsened.

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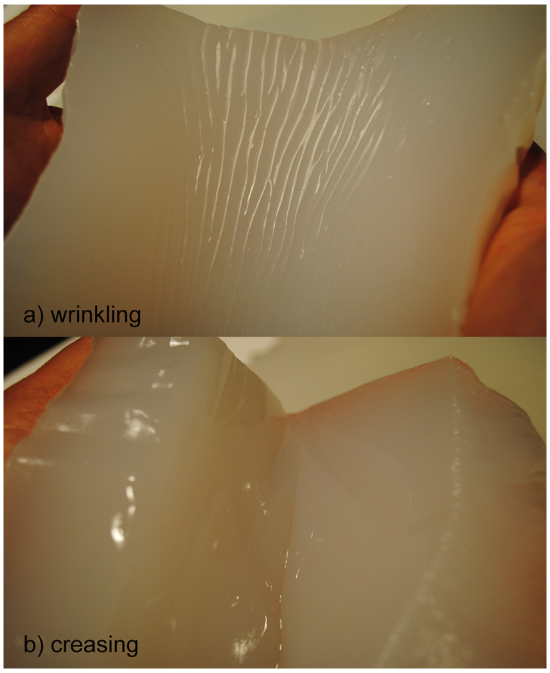

FIG. 2. Bending-induced instability in a popular Chinese food, Liang Fen (a starch gel). A hot solution was poured into a large tray and was left at room temperature for hours to form a gel. On the top surface of the gel, a thin stiff skin formed due to the evaporation of water. (a) When the gel was bent to compress the top surface, multiple wrinkles formed. (b) When the gel was bent to compress the bottom surface, a single crease formed. (Courtesy of Denian Zhuang).

solvent (Fig. 4). When the gel is in the reference state, which we take to be the dry polymer, an element of the network occupies a location of coordinate $\mathbf{X}$. Let $dV(\mathbf{X})$ be an element of volume, $dA(\mathbf{X})$ an element of area, and $\mathrm{N}(\mathbf{X})$ the unit vector normal to the element of area. In a swollen state, the element $\mathbf{X}$ of the network moves to a new location of coordinate $\mathbf{x}$. The function $\mathbf{x}(\mathbf{X})$ specifies the deformation of the gel. The deformation gradient is defined as

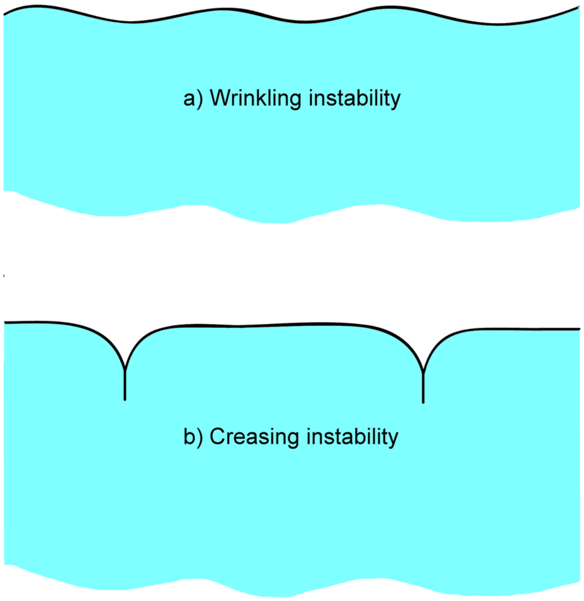

FIG. 3. Schematics of two types of surface instability: (a) wrinkles and (b) creases.

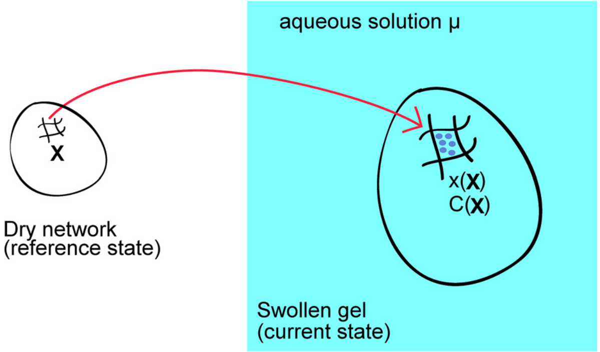

FIG. 4. Each element of the network is marked by its coordinate $\mathbf{X}$, when the network is in the reference state, which is taken to be the dry polymer. When the network absorbs the solvent and swells, the element of the network moves to a new location of coordinate $\mathbf{x}$. The field of deformation, $\mathbf{x}(\mathbf{X})$, and the field of concentration of the solvent, $C(\mathbf{X})$, together describe the state of the gel.

$$F_{iK}(\mathbf{X}) = \frac{\partial x_i(\mathbf{X})}{\partial X_K}. \tag{2.1}$$

Let C be the nominal concentration of the solvent in the gel—that is, $CdV(\mathbf{X})$ is the number of solvent molecules in the element of volume. The function $C(\mathbf{X})$ specifies the distribution of the solvent in the gel. The two functions $\mathbf{x}(\mathbf{X})$ and $C(\mathbf{X})$ together specify the state of the gel.

Let $s_{iK}(\mathbf{X})$ be the field of nominal stress, $B_i(\mathbf{X})$ be the nominal body force, and $T_i(\mathbf{X})$ be the nominal traction on the surface. The balance of forces requires that

$$\frac{\partial s_{iK}(\mathbf{X})}{\partial X_K} + B_i(\mathbf{X}) = 0 \tag{2.2}$$

in the volume of the gel, and

$$s_{iK}(\mathbf{X})N_K(\mathbf{X}) = T_i(\mathbf{X}) \tag{2.3}$$

on the surface of the gel, where the traction is prescribed.

The gel is submerged in an environment, which may contain many species of molecules, as well as the solvent molecules. The setup is such that the gel and the environment only exchange the solvent. When the gel equilibrates with the environment, the chemical potential of the solvent is the same everywhere, which we denote as μ. Our analysis assumes that both the temperature and the chemical potential of the solvent are held constant. Let W be the nominal Helmholtz free energy density of the gel (i.e., the Helmholtz free energy of the gel divided by the volume of the dry polymer). Considering the Helmholtz free energy of the gel and that of the environment, a combined free energy is defined as a function of the deformation gradient and the chemical potential of the solvent, $\hat{W} = W - \mu C$. In a state of thermodynamic equilibrium, the change in the combined free energy equals the work done by the stresses

$$\delta\hat{W} = s_{iK}\delta F_{iK}. \tag{2.4}$$

The equality holds for arbitrary variation of the all nine components of the deformation gradient. The gel is characterized by a function $\hat{W}(\mathbf{F}, \mu)$. The condition of equilibrium (2.4) is equivalent to

$$s_{iK} = \frac{\partial \hat{W}(\mathbf{F},\mu)}{\partial F_{iK}}. \tag{2.5}$$

This expression gives the equations of state once the function $\hat{W}(\mathbf{F},\mu)$ is prescribed.

As a specific material model, the function $\hat{W}(\mathbf{F},\mu)$ is prescribed as follows. The free energy is the sum of three contributions[9]

$$\hat{W}(\mathbf{F},\mu) = W_{stretch} + W_{mix} - \mu C. \tag{2.6}$$

The free energy of stretching follows the Gaussian-chain model:

$$W_s = \frac{1}{2} N k_B T [F_{iK}F_{iK} - 3 - 2\log(\det \mathbf{F})], \tag{2.7}$$

where N is the number of polymer chains per volume of dry polymer, k_BT is the absolute temperate in the unit of energy. The free energy of mixing follows the Flory-Huggins model:[10,11]

$$W_{mix} = k_B T \left[C \log \frac{\Omega C}{1+\Omega C} + \frac{\chi C}{1+\Omega C} \right], \tag{2.8}$$

where Ω is the volume of a solvent molecule, and χ is a dimensionless parameter measuring the enthalpy of mixing. It is commonly assumed that the volume of the gel changes only by absorption or desorption of the solvent molecules

$$\det \mathbf{F} = \Omega C + 1. \tag{2.9}$$

A combination of (2.6)–(2.9) gives the equations of state

$$\begin{aligned} s_{iK} = {} & N k_B T (F_{iK} - H_{iK}) + \frac{k_B T}{\Omega}\left[(\det \mathbf{F}) \log\left(1 - \frac{1}{\det \mathbf{F}}\right)\right. \\ & \left. + 1 + \frac{\chi}{\det \mathbf{F}} - \frac{\mu}{k_B T}(\det \mathbf{F})\right] H_{iK}, \end{aligned} \tag{2.10}$$

where $H_{iK} \det \mathbf{F} = \partial \det \mathbf{F} / \partial F_{iK} = \frac{1}{2} e_{ijk} e_{KLM} F_{jL} F_{kM}$.

The kinematic equation (2.1), the conditions of force balance (2.2), and the equations of state (2.10), along with boundary conditions, constitute a boundary-value problem that governs the state of equilibrium of a gel submerged in an environment. The governing equations take the same form as those for compressible hyperelastic solids.

Now consider a layer of a gel attached to a rigid substrate (Fig. 5). As fabricated, the gel is partially swollen with an isotropic initial swelling ratio, $\lambda_1 = \lambda_2 = \lambda_3 = \lambda_{pre}$. Immersed in a solvent-containing environment, the gel swells further in the thickness direction. We assume the thickness of the layer to be much smaller than the in-plane dimensions and ignore the edge effect. The constrained swelling of the gel layer results in an equal-biaxial compressive stress, while the stress in the thickness direction vanishes. For a given λ_{pre}, the swelling ratio in the thickness direction, λ_3, is a function of the chemical potential[12]

$$\begin{aligned} \frac{\mu}{k_B T} = {} & \frac{N\Omega}{\lambda_{pre}^2}\left(\lambda_3 - \frac{1}{\lambda_3}\right) + \log\left(1 - \frac{1}{\lambda_{pre}^2 \lambda_3}\right) \\ & + \frac{1}{\lambda_{pre}^2 \lambda_3} + \frac{\chi}{(\lambda_{pre}^2 \lambda_3)^2}. \end{aligned} \tag{2.11}$$

The environment is taken to be a pure solvent, in which the chemical potential is set to be zero, $\mu = 0$. The equilibrium swelling ratio λ_3 decreases as any one of the three parameters, λ_{pre}, $N\Omega$, and χ, increases (Fig. 5).

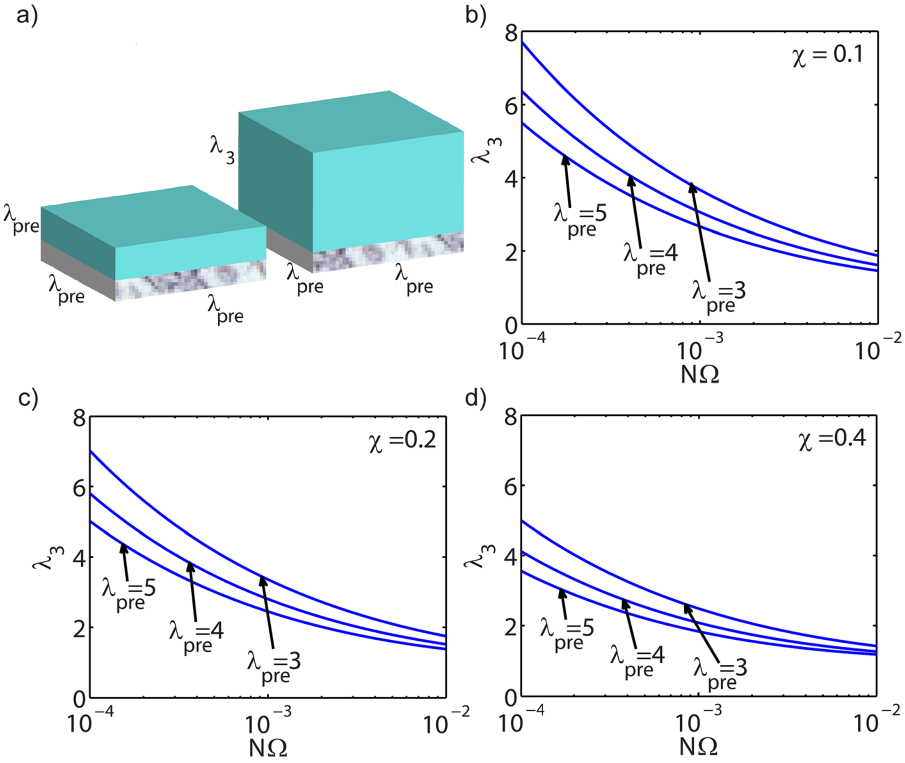

FIG. 5. A gel is attached to a rigid substrate. The thickness of the gel is much smaller than the in-plane dimensions. In a homogeneous state, the gel is constrained by the substrate in the in-plane dimensions, and swells in the thickness direction. The amount of swelling λ_3 depends on the crosslink density $N\Omega$, the Flory-Huggins parameter χ, and the prestretch λ_{pre}.

III. CRITICAL CONDITION FOR THE ONSET OF WRINKLES

An analysis has been carried out by Kang and Huang[13] to determine the condition for the onset of wrinkles for the case $\lambda_1 = \lambda_2 = 1$. Here, we carry out the analysis for a gel with in-plane pre-stretches. In this analysis, the control parameters ($N\Omega$, χ, and the pre-stretches) are fixed, and the homogeneous state is perturbed with a field of small deformation. Consider a state of finite deformation specified by the deformation $x_i^0(\mathbf{X})$, deformation gradient $F_{iK}^0(\mathbf{X})$, nominal stress $s_{iK}^0(\mathbf{X})$, and traction $T_i^0(\mathbf{X})$. Perturb the state of finite deformation with a state of infinitesimal deformation

$$x_i = x_i^0 + \tilde{x}_i, \tag{3.1}$$

$$F_{iK} = F_{iK}^0 + \tilde{F}_{iK}, \tag{3.2}$$

$$s_{iK} = s_{iK}^0 + \tilde{s}_{iK}, \tag{3.3}$$

$$T_i = T_i^0 + \tilde{T}_i. \tag{3.4}$$

By Eqs. (2.1)–(2.3), we have

$$\tilde{F}_{iK} = \frac{\partial \tilde{x}_i(\mathbf{X})}{\partial X_K}, \tag{3.5}$$

$$\frac{\partial \tilde{s}_{iK}}{\partial X_K} = 0, \tag{3.6}$$

$$\tilde{s}_{iK} N_K = \tilde{T}_i. \tag{3.7}$$

This set of Eqs. (3.5)–(3.7) is linear in the incremental fields.

Expanding Eq. (2.5) in the Taylor series and keeping only the linear term, we obtain that

$$\tilde{s}_{iK} = \frac{\partial^2 \hat{W}}{\partial F_{iK} \partial F_{jL}} \tilde{F}_{jL} = C_{iKjL}(\mathbf{F}^0, \mu) \tilde{F}_{jL}, \tag{3.8}$$

where C_{iKjL} is the tensor of tangent moduli. Further assume that the finite deformation before the perturbation is homogenous, so that C_{iKjL} is a constant tensor. The tangent moduli depend on $N\Omega$, χ, and prestretches, as listed in Appendix A. A combination of (3.5), (3.6), and (3.8) gives that

$$C_{iKjL} \frac{\partial \tilde{x}_j(\mathbf{X})}{\partial X_L \partial X_K} = 0. \tag{3.9}$$

The infinitesimal incremental displacement $\tilde{\mathbf{x}}(\mathbf{X})$ is governed by this linear partial differential equation, along with the homogeneous boundary conditions (namely, the increment in the traction vanishes on the surface of the gel, and the increment in the displacement vanishes at the interface between the gel and the rigid substrate). This analysis leads to an eigenvalue problem. The trivial solution corresponds to a homogeneous state, while the nontrivial solutions correspond to wrinkled states. The characteristic equation determines the critical condition for the onset of wrinkles, and the associated eigenvector describes a mode of deformation. The amplitude of the deformation, however, is not determined by this analysis.

For a two-dimensional problem, with geometry and external loading invariant in the direction normal to (X_1, X_3)-plane, the general solution to the linearized boundary-value problem is given in the Stroh formalism (Appendix A). We then assume that the wavelength is small compared with the thickness of the gel, so that the gel is taken to be semi-infinite in the analysis. Solution to this problem is obtained by using the method of analytic functions (Appendix B). The critical condition for the onset of wrinkles is written in terms of the homogeneous swelling ratios as

$$\frac{(\lambda_1^2 + \lambda_3^2)^2}{\lambda_1 \lambda_3} - 4\lambda_3^2 \sqrt{\frac{\lambda_1^2 + \zeta}{\lambda_3^2 + \zeta}} = 0 \tag{3.10}$$

with

$$\zeta = \frac{1}{N\Omega}\left(\frac{1}{\lambda_1\lambda_2\lambda_3 - 1} - \frac{2\chi}{\lambda_1\lambda_2\lambda_3}\right) + 1. \tag{3.11}$$

For a given prestretch $\lambda_1 = \lambda_2 = \lambda_{pre}$, the critical swelling ratio in the thickness direction, λ_3, is obtained from (3.10), with which the critical chemical potential can be found by (2.11). When the in-plane prestretch $\lambda_1 = \lambda_2 = 1$, (3.10) recovers the critical condition obtained by Kang and Huang.[11] An alternative analysis was presented by Kang[14] using the method of Fourier transform, which predicted the same critical condition for wrinkling of a swollen gel layer under an equal-biaxial pre-stretch.

By combining (3.10) and (2.11) and setting the chemical potential to be zero for the equilibrium swelling, the critical condition for the onset of wrinkles is obtained as a relation between the three parameters: $N\Omega$, χ, and λ_{pre}. For each χ, the critical pre-stretch decreases with increasing $N\Omega$ (Fig. 6). In this calculation, λ_{pre} is the pre-stretch in two lateral directions, which may be induced by swelling or mechanical stretching (compression). For large $N\Omega$ ($\sim$1), the critical pre-stretch approaches 0.666 as predicted by Biot[15] for rubber under equi-biaxial compression. In this case, the polymer

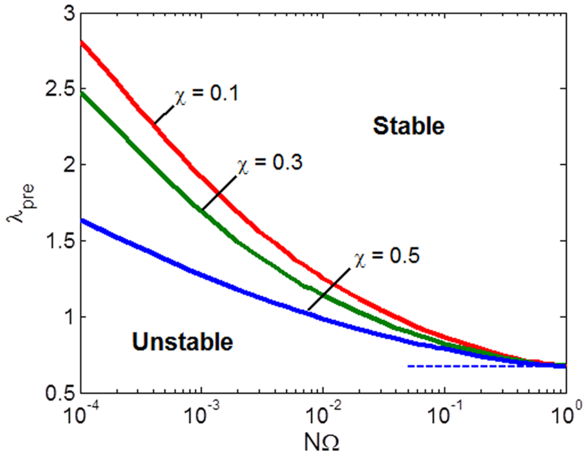

FIG. 6. Critical prestretch for the onset of wrinkles. The gel is stable against wrinkling, when the prestretch is greater than the critical value. For large $N\Omega$, the critical prestretch approaches 0.666 (the dashed line) as predicted by Biot (1963) for rubber under equal-biaxial compression.

network is highly crosslinked so that it cannot absorb much solvent and hence behaves like a rubber in the dry state.

IV. CRITICAL CONDITION FOR THE ONSET OF CREASES

A crease sets in when the deformation deviates from the homogenous state by a field of strain large in amplitude, but infinitesimal in space. The critical condition for the onset of the crease cannot be predicted by perturbing the homogeneous state with a field of small deformation. In this section, we present two numerical methods to predict the onset of creases in a gel attached to a rigid substrate.

The first method is based on an energy consideration.[16] Consider a gel in a homogeneous state and a creased state (Fig. 7). The free energy of the swollen gel in the homogenous state can be calculated analytically as described in Sec. II. The creased state is created by imposing a boundary condition with prescribed horizontal displacements that bring part of the surface OA' into contact with OA. The length of AA', L, is set to be small compared to the thickness of the gel H, say, $L/H \approx 1/100$, so that the depth of the crease is the only relevant length scale in the problem. Let ΔU be the free energy per unit thickness of the creased gel minus that in the state of homogenous swelling. A dimensional consideration dictates that

$$\Delta U = \frac{k_B T L^2}{\Omega} f_C(\lambda_{pre}, N\Omega, \chi), \tag{4.1}$$

where $f_C(\lambda_{pre}, N\Omega, \chi)$ is a dimensionless function to be calculated. When $\Delta U > 0$, the homogenously swollen state has lower free energy. When $\Delta U < 0$, the creased state has lower free energy. The critical condition is, thus, established by setting $\Delta U = 0$, namely,

$$f_C(\lambda_{pre}, N\Omega, \chi) = 0. \tag{4.2}$$

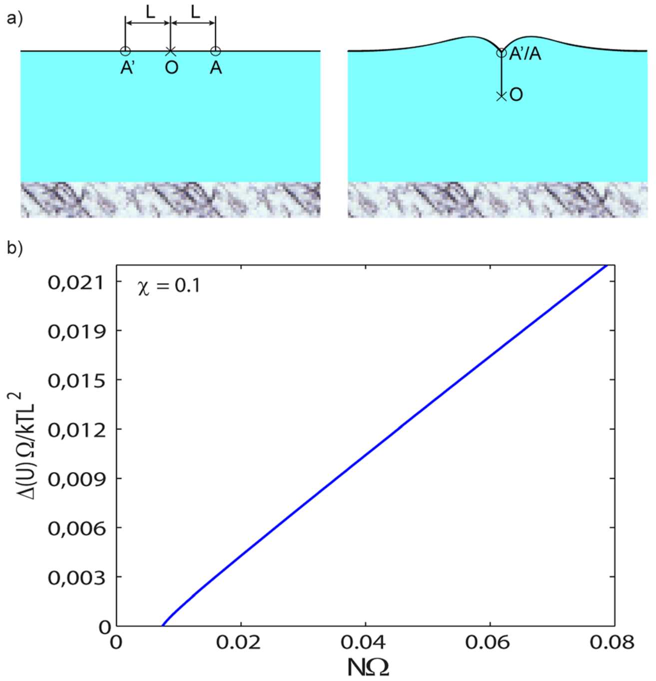

FIG. 7. Finite-element calculation of creasing of a gel attached to a rigid substrate. (a) Schematics of a homogeneous state of the swollen gel and a creased state. (b) The deference between the energy of the creased state and that of the homogeneous state is plotted as a function of $N\Omega$. ($\chi = 0.1$ and $\lambda_{pre} = 1.55$).

We note that the critical condition (4.2) is independent of the prescribed crease size (L) or the gel thickness H.

We calculate the free energy of the creased gel by using a finite element method to equilibrate the gel.[12] Fig. 7(b) shows one plot of the function $f_C(\lambda_{pre}, N\Omega, \chi)$ for $\lambda_{pre} = 1.55$ and $\chi = 0.1$. The function approaches zero at a critical value of $N\Omega$, which predicts the critical crosslink density. For a gel with the crosslink density lower than the critical value, the homogeneous swollen state is unstable giving rise to surface creases that lower the free energy of the swollen gel. Similarly, for given parameters $N\Omega$ and χ, a critical prestretch may be predicted. For given $N\Omega$ and λ_{pre}, a critical value for χ may be predicted.

The above method cannot continue the calculation beyond the critical condition. Alternatively, we use a second method, introduced recently by Cai *et al.*[17,18] and Jin *et al.*,[19] to simulate the initiation and growth a crease. A small defect is introduced to specify the location of the crease. In particular, a quarter of a circle of a small radius, a, is placed on the surface of the swollen gel in the finite element model (Fig. 8). To minimize the effect of the size of the defect, the defect is made much smaller than the layer thickness H, say $a/H \approx 1/100$. Moreover, to resolve the field close to the tip of the crease and to minimize the effect of mesh size, the size of the finite elements around the defect is made much smaller than the defect. Fig. 8(b) shows the equilibrated state with a deep crease obtained by the finite element method.[12] The depth of the crease at the equilibrium state ($\mu = 0$) is determined from the contact length, which is plotted as a function of $N\Omega$ in Fig. 8(a) for the same λ_{pre} and χ as in Fig. 7(b) The depth of crease decreases with increasing $N\Omega$. Beyond a critical value of $N\Omega$, the depth is essentially zero. The critical value for $N\Omega$ obtained from the energy method (Fig. 7(b)) is marked in Fig. 8(a), which is consistent with the transition point from positive crease depth to zero crease depth.

Therefore, both methods can be used to predict the critical condition for the onset of creases. While the energy method is more convenient to quantitatively determine the critical value, the second method enables post-instability analysis to predict the profile of deep creases as shown in Fig. 8(b). It is observed in Fig. 8(b) that the solvent concentration is the lowest in the vicinity of the crease tip. This is consistent with the previous calculations by Kang and Huang,[14] who showed that the in-plane compressive stress is relatively low at the crease tip. With the inhomogeneous fields of solvent concentration and stress, the total free energy of the creased state is lower than the homogeneous state of swelling. Further analysis of the post-instability creasing behavior is left for future studies.

V. COMPARISON AND DISCUSSION

The critical condition for the onset of wrinkles in a biaxially constrained swollen gel is given by the combination of

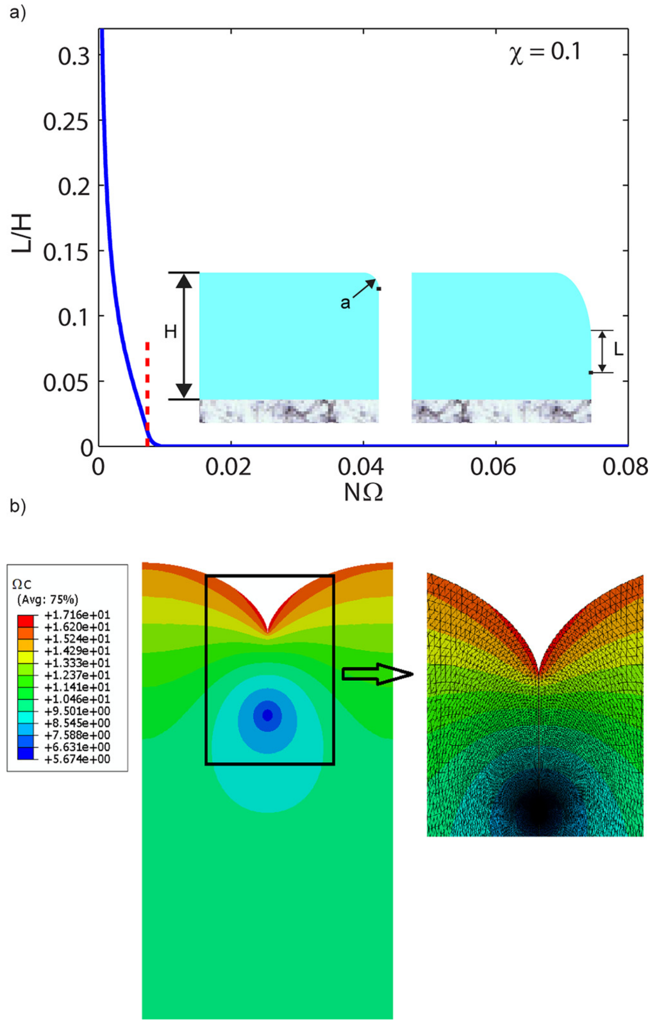

FIG. 8. Finite-element simulation of the formation of a crease from an initial defect. (a) The equilibrium contact length at the creased region is plotted as a function of $N\Omega$. ($\chi = 0.1$ and $\lambda_{pre} = 1.55$) The red dashed line denotes the critical value of $N\Omega$ obtained from the energy method in Fig. 6. (b) Contour plot of the solvent concentration ΩC around the crease.

(2.11) and (3.10), and that of creases is given in (4.2). Fig. 9(b) compares the critical prestretch λ_{pre}, plotted as a function of $N\Omega$ for different values of χ. The surface of a swollen gel is unstable if the pre-stretch is less than the critical value. The critical prestretch for creasing is larger than that for wrinkling. In other words, it takes a larger prestretch to stabilize the swollen gel against creasing than it takes against wrinkling. For both creasing and wrinkling, the critical prestretch λ_{pre} decreases with increasing $N\Omega$ and χ. This can be understood as follows: the equilibrium swelling ratio of the gel in the homogeneous state decreases with increasing $N\Omega$ or χ, and as a result the prestretch λ_{pre} required to stabilize the swollen gel decreases. As shown in Fig. 6, for some $N\Omega$ and χ the critical prestretch is less than 1, meaning that the swollen gel is stable without any prestretch but becomes unstable if the prestretch is instead compressive ($\lambda_{pre} < 1$). In the limiting case, when $N\Omega$ or χ is very large, the polymer network cannot absorb much of the solvent and thus behaves like a dry elastomer. As predicted in the previous studies,[15,16] for an elastomer under equi-biaxial compression, the critical conditions for the onset of wrinkles and creasing are $\lambda_{pre} = 0.666$ and $\lambda_{pre} = 0.749$, respectively.

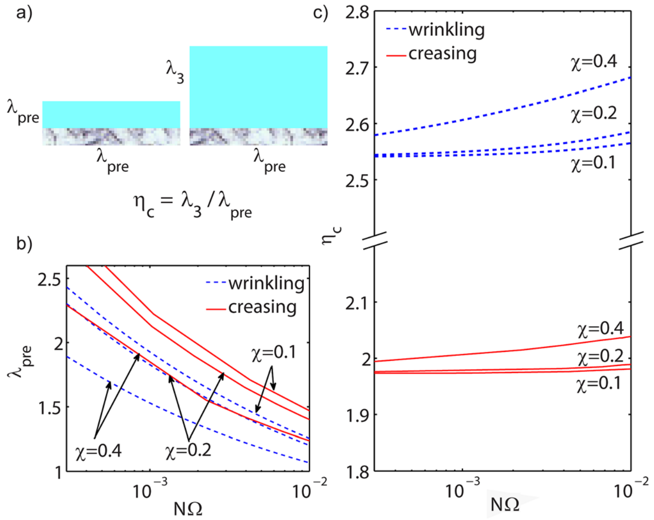

FIG. 9. Comparison of the critical conditions for the onset of wrinkles and creases. (a) A gel is attached to a rigid substrate in a state of isotropic prestretch λ_{pre}, and swells in the thickness direction to a stretch of λ_3. (b) The critical prestretch varies with $N\Omega$ and χ. (c) The critical swelling ratio, $\eta_c = \lambda_3/\lambda_{pre}$, varies with $N\Omega$ and χ. The red solid lines are the critical conditions for the onset of creases, and the blue dashed lines are the critical conditions for the onset of wrinkles.

Experimentally, the critical conditions for surface instability of swollen gels are often reported as the critical thickness ratio between the swollen gel and the gel in the initial state. Denote the ratio of the two thicknesses as, $\eta = \lambda_3/\lambda_{pre}$. Figure 9(c) plots the critical ratio η_c for both wrinkling and creasing as a function of $N\Omega$ for different χ. Clearly, the critical swelling ratio required for creasing is considerably lower than for wrinkling in all cases. In general, the critical swelling ratio depends on the material parameters of the gel ($N\Omega$ and χ). The reported critical swelling ratios from experiments range from around 2 to 3.7.[1,20,21]

Wrinkling and creasing as two types of surface instability have also been studied for elastomers under mechanical compression.[7,15,21] It was found that the critical compressive strain for the onset of creases is lower than that for the onset of wrinkles. The connection between the two types of instability has been studied recently by Cao and Hutchinson.[22] By a post-bifurcation analysis, they showed that the wrinkling mode is highly unstable and imperfection sensitive. Consequently, a tiny initial imperfection can trigger the onset of wrinkling instability at a lower compressive strain and the wrinkles quickly collapse into a crease. As such wrinkling was suggested as one pathway to formation of creases in elastomers. Similar connection may be expected for wrinkling and creasing in swollen gels. Indeed, numerical simulations by Kang and Huang[13] showed that an initial undulation of the surface of a gel may evolve into wrinkles and collapse into creases during swelling. However, analysis of imperfection sensitivity for surface instability in swollen gels has not been reported.

Finally, we note that the swollen gel is assumed to be in a homogeneous state before the onset of surface instability in the present study. As a result, the critical condition is independent of any length scale. In practice, however, the surface instability may be regulated by a length scale. For example, in Fig. 1, the transport kinetics defines a length scale that increases with time. In Fig. 2(a), the thickness of the skin layer dictates the wrinkle wavelength. A length scale can also be introduced by considering the effect of surface tension.[23] Experimentally, a wide range of surface instability patterns have been observed by controlling the gradient of crosslink density in the polymer network of gel films,[24] in which case the length scale is defined by the graded material property. The intriguing instability patterns call for further studies that integrate mechanics with soft matter physics.

VI. CONCLUDING REMARKS

We calculate the critical conditions for the onset of wrinkles and creases in a swollen gel attached to a rigid substrate. The critical swelling ratio for the onset of creases is found to be considerably lower than that of wrinkles. This theoretical finding is consistent with experimental observations. While creases are readily observed during swelling, we are unaware of any experimental evidence of wrinkles localized on the surface during swelling, except for incidences in which the gel has thickness-graded properties. It is hoped that the approaches described here will be useful for determining the critical conditions for the onset of creases and wrinkles in other configurations and materials.

ACKNOWLEDGMENTS

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APPENDIX A: STROH FORMALISM

Equation (3.9) is a set of three second-order linear partial differential equations, the form of which is identical to that of anisotropic elasticity. Consequently, the present problem can be solved by adapting the Stroh formalism of anisotropic elasticity.[25,26] The solution of the partial differential equations (3.9) is given by an arbitrary function of a linear combination of the variables X_1 and X_3

$$\tilde{x}_k(X_1, X_3) = a_k f(X_1 + pX_3), \qquad \text{(A1)}$$

where a_k is a vector, p is a number, and $f(z)$ is an analytic function of the variable z. Inserting (A1) into (3.9), one obtains that

$$\left[C_{i1k1} + p(C_{i1k3} + C_{i3k1}) + p^2 C_{i3k3}\right] a_k \frac{d^2 f(z)}{dz^2} = 0. \qquad \text{(A2)}$$

We are interested in nontrivial solutions in that $d^2 f(z)/dz^2 \neq 0$ and not all components of a_k vanish. Consequently, (A2) constitutes an eigenvalue problem, with a_k as an eigenvector, and p as an eigenvalue determined as a root of the sixth-order polynomial equation

$$\det[C_{i1k1} + p(C_{i1k3} + C_{i3k1}) + p^2 C_{i3k3}] = 0. \qquad \text{(A3)}$$

Eshelby *et al.*[26] proved that Eq. (A3) has no real root, so that the roots for the equation are complex conjugate pairs. We denote p_j $(j = 1, 2, 3)$ as the three distinct roots with positive imaginary part. The eigenvector a_k corresponding to p_j is denoted by A_{kj}. The field $\tilde{x}_k(X_1, X_3)$ is real-valued. Therefore, a general expression for the displacement can be written as

$$\tilde{x}_i = 2\,\mathrm{Re}\left[\sum_{j=1}^{3} A_{ij} f_j(z_j)\right], \qquad \text{(A4)}$$

where $z_j = X_1 + p_j X_3$.

Inserting (A4) into Eq. (3.8), we find that the incremental nominal stress $\tilde{s}_{iK}$, and the incremental resultant force on an arc $\tilde{R}_i$ (the medium is kept on the left-hand side as an observer travels in the positive direction of the arc) can be represented as

$$\tilde{s}_{i3} = 2\,\mathrm{Re}\left[\sum_{j=1}^{3} L_{ij} f'_j(z_j)\right], \qquad \text{(A5)}$$

$$\tilde{s}_{i1} = -2\,\mathrm{Re}\left[\sum_{j=1}^{3} L_{ij} p_j f'_j(z_j)\right], \qquad \text{(A6)}$$

$$\tilde{R}_i = -2\,\mathrm{Re}\left[\sum_{j=1}^{3} L_{ij} f_j(z_j)\right]. \qquad \text{(A7)}$$

The incremental resultant force is defined by an integral, $\tilde{R}_i(X_1, X_3) = \int_C (\tilde{s}_{i1} n_1 + \tilde{s}_{i3} n_3) dC$, where the integration is carried out from infinity to the point (X_1, X_3), and n_1 and n_3 are the components of the unit normal to C. By comparing (A5) and (A6) with (3.8), the matrix $\mathbf{L}$ is obtained as

$$L_{i\alpha} = \sum_{k=1}^{3} [C_{i3k1} + p_\alpha C_{i3k3}] A_{k\alpha}. \qquad \text{(A8)}$$

Given the tensor C_{iKjL}, Eq. (A4) gives the form of the solution to the partial differential equations (3.9) without invoking any boundary conditions. The three functions $f_1(z_1), f_2(z_2)$, and $f_3(z_3)$ are to be determined by the boundary conditions.

We now calculate the tangent moduli C_{iKjL} for the gel. Taking derivative of (2.10), we obtain the tensor of tangent moduli

$$C_{iKjL} = Nk_B T\left(\delta_{ij}\delta_{KL} + (\zeta - \psi) H^0_{iL} H^0_{jK} + \psi H^0_{jL} H^0_{iK}\right), \qquad \text{(A9)}$$

with

$$\zeta = \frac{1}{N\Omega}\left(\frac{1}{J-1} - \frac{2\chi}{J}\right) + 1, \qquad \text{(A10)}$$

and

$$\psi = \frac{J}{N\Omega}\left(\log\left(1-\frac{1}{J}\right)+\frac{1}{J-1}-\frac{\chi}{J^2}-\frac{\mu}{k_BT}\right), \tag{A11}$$

where $J = \det\mathbf{F}^0$. The field of finite deformation before perturbation is homogeneous, and the principal stretches are in the directions coinciding with X_1, X_2, and X_3. Consequently, $\mathbf{F}^0 = diag(\lambda_1,\lambda_2,\lambda_3)$, $\mathbf{H}^0 = diag(1/\lambda_1, 1/\lambda_2, 1/\lambda_3)$, $J = \lambda_1\lambda_2\lambda_3$, and the tangent moduli (A9) reduce to the following nonzero elements:

$$C_{1111} = Nk_BT\left(1+\frac{\zeta}{\lambda_1^2}\right), \quad C_{2222} = Nk_BT\left(1+\frac{\zeta}{\lambda_2^2}\right),$$
$$C_{3333} = Nk_BT\left(1+\frac{\zeta}{\lambda_3^2}\right), \tag{A12}$$

$$C_{1212} = C_{2121} = C_{1313} = C_{3131} = C_{3232} = C_{2323} = Nk_BT, \tag{A13}$$

$$C_{1122} = C_{2211} = \frac{Nk_BT}{\lambda_1\lambda_2}\psi, \quad C_{1133} = C_{3311} = \frac{Nk_BT}{\lambda_1\lambda_3}\psi,$$
$$C_{2233} = C_{3322} = \frac{Nk_BT}{\lambda_2\lambda_3}\psi, \tag{A14}$$

$$C_{2112} = C_{1221} = \frac{Nk_BT}{\lambda_1\lambda_2}(\zeta-\psi),$$
$$C_{3113} = C_{1331} = \frac{Nk_BT}{\lambda_1\lambda_3}(\zeta-\psi), \tag{A15}$$
$$C_{3223} = C_{2332} = \frac{Nk_BT}{\lambda_2\lambda_3}(\zeta-\psi).$$

We next solve the eigenvalue problem in the Stroh formalism. The (X_1, X_3)-plane is a mirror plane, so that the in-plane deformation and antiplane deformation are decoupled. We focus on the in-plane deformation described by two analytic functions $f_1(z_1)$ and $f_3(z_3)$, with $z_1 = X_1 + p_1X_3$ and $z_3 = X_1 + p_3X_3$. The complex numbers p_1 and p_3 are determined by (A3), which is specialized as

$$\left(\left(1+\frac{\zeta}{\lambda_3^2}\right)p^2 + \left(1+\frac{\zeta}{\lambda_1^2}\right)\right)(p^2+1) = 0. \tag{A16}$$

The two roots with positive imaginary part of the above equation are

$$p_1 = i\sqrt{\frac{\lambda_3^2(\lambda_1^2+\zeta)}{\lambda_1^2(\lambda_3^2+\zeta)}}, \quad p_3 = i. \tag{A17}$$

All the 3×3 matrices introduced before reduce to 2×2 matrices for the in-plane deformation. Keeping the same notation, we obtain that

$$A_{11} = i, \quad A_{13} = i, \quad A_{31} = -\sqrt{\frac{\lambda_1^2+\zeta}{\lambda_3^2+\zeta}}, \quad A_{33} = -\frac{\lambda_3}{\lambda_1}; \tag{A18}$$

$$L_{11} = -2Nk_BT\sqrt{\frac{\lambda_3^2(\lambda_1^2+\zeta)}{\lambda_1^2(\lambda_3^2+\zeta)}}, \quad L_{31} = -iNk_BT\left(\frac{\lambda_1^2+\lambda_3^2}{\lambda_1\lambda_3}\right),$$
$$L_{13} = -Nk_BT\left(1+\frac{\lambda_3^2}{\lambda_1^2}\right), \quad L_{33} = -2iNk_BT\frac{\lambda_3}{\lambda_1}. \tag{A19}$$

APPENDIX B: CRITICAL CONDITION FOR THE ONSET OF WRINKLES

The three functions $f_1(z_1)$, $f_2(z_2)$, and $f_3(z_3)$ are to be determined by the boundary conditions. We now derive the critical condition for the onset of wrinkles using the one-complex-variable method of Suo.[27] Let z be a complex variable of the form $z = X_1 + qX_3$, with q being an arbitrary complex number with a positive imaginary part. Write

$$\mathbf{f}(z) = [f_1(z), f_2(z), f_3(z)]^T. \tag{B1}$$

The function $\mathbf{f}(z)$ describes the wrinkled state. The surface of the gel ($X_3 = 0$) is traction-free, so that (A7) reduces to

$$\mathbf{Lf}(X_1) + \bar{\mathbf{L}}\bar{\mathbf{f}}(X_1) = 0. \tag{B2}$$

This equation sets the boundary condition for the function $\mathbf{f}(z)$. It can be shown that this condition is equivalent to that by setting $\tilde{s}_{i3} = 0$ everywhere on the surface ($n_1 = 0$ and $n_3 = 1$).

The boundary-value problem is solved as follows. Assume that the gel occupies the lower half plane ($X_3 \le 0$). Because no singularity is present in the gel, $\mathbf{Lf}(z)$ is a function analytic in the lower half plane. Consequently, $\bar{\mathbf{L}}\bar{\mathbf{f}}(z)$ is a function analytic in the upper half plane. By the theorem of analytic continuation, the boundary condition (B2) requires that both functions be analytic in the entire plane. The wrinkles are disturbance localized on the surface of the gel, so that the analytic functions vanish as $|z| \to \infty$. The only function analytic in the entire plane and vanishing as $|z| \to \infty$ is the function being zero everywhere. Consequently, the solution to the boundary-value problem (B2) is

$$\mathbf{Lf}(z) = 0. \tag{B3}$$

Equations analogous to (B3) have been used to study surface wave in anisotropic elastic materials (e.g., Lothe and Barnett[28]).

Equation (B3) is an eigenvalue problem. A nontrivial solution of $\mathbf{f}(z)$ exists if and only if

$$\det\mathbf{L} = 0. \tag{B4}$$

For the in-plane deformation of a swollen gel, a combination of (A19) and (B4) gives a single solution (3.10). Denote $\mathbf{e}$ as the eigenvector solved from the eigenvalue problem $\mathbf{Le} = 0$. The wrinkled state is given as

$$\mathbf{f}(z) = w(z)\mathbf{e}, \tag{B5}$$

where $w(z)$ is an arbitrary scalar-valued function.

Equation (B4) gives the critical condition for the onset of wrinkles, while (B5) gives the shape of the wrinkles. This analysis assumes that the gel occupies a half space, and the critical condition is found to be the same for wrinkles of any shape. For the matrix **L** specified by (A19), the critical condition (B4) reduces to

$$\frac{(\lambda_1^2+\lambda_3^2)^2}{\lambda_1\lambda_3} - 4\lambda_3^2\sqrt{\frac{\lambda_1^2+\zeta}{\lambda_3^2+\zeta}} = 0, \tag{B6}$$

and the eigenvector is

$$\mathbf{e} = [2\lambda_3^2,\ -(\lambda_1^2+\lambda_3^2)]^T. \tag{B7}$$

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