Evolution of Surface Patterns on Swelling Gels

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A simple model, describing a network of springs moving against friction, is used to study the evolution of surface patterns on a gel undergoing uniaxial expansion. The nonlinear growth equation obtained adequately describes the key experimental observations, such as the scaling of the typical size of patterns and the formation of cusps. The dynamics is carried on a computer, and the patterns obtained are in qualitative agreement with experiments.

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Complex physical and biological patterns can evolve from simple underlying equations. Linear stabilities, interaction of different modes through nonlinearities, are some of the ingredients for the formation of such patterns. These phenomena have been extensively studied in the context of formation of dendrites and snowflakes.[1] Here we examine patterns that form on surfaces of expanding gels. Observed first experimentally by Tanaka[2] these patterns are present on surfaces of gels undergoing a discontinuous volume expansion[3] (induced by changes in temperature, pH, etc.). As the gel swells, initially very fine patterns appear on an originally smooth surface. With further expansion, the units of the pattern coalesce, forming similar patterns at successively larger length scales. A cross section of the gel reveals that the pattern is composed of smooth arcs coming together with cusp-shaped singularities. From the top, these singularities form a honeycomblike network. The general underlying mechanism for formation of such patterns has been correctly attributed to mechanical (elastic) instabilities by a number of authors[4-6] from analysis of equilibrium theories of various complexities. However, the mechanisms for the taming of the mechanical instabilities and the formation of cusp structures have not been investigated; a complete dynamic description of the evolution of these surface patterns has been lacking.

Here we introduce a very simple model (a network of springs expanding against friction in $1+1$ dimensions) for the gel and show that it can account for all of the key observed phenomena concerning these patterns. After making some reasonable assumptions regarding the strains and the taming of instabilities by interactions, we can actually follow the evolution of patterns on a computer. The basic results in $1+1$ dimensions are a swollen layer of thickness $l(t)$ (measured from the surface of the gel) growing diffusively with time; for large enough expansion, a band of unstable modes developing for transverse fluctuations over a range of wavelengths proportional to $l(t)$; formation of cusps as a result of instabilities and lateral motion of the particles; and the hierarchy of cusp evolution. Simple extension of the model can also account for patterns in $2+1$ dimensions.

We model a rectangular slab of gel by a square lattice of beads connected by harmonic springs (of spring constant K) moving in a viscous medium (of frictional coefficient f). Swelling is initiated by a change in the equilibrium spring length from 1 to E at $t=0$. In the experiment this change is induced by the variation of temperature or pH of the environment, and $E\sim 10$ is quite typical. Let $\mathbf{x}=(x_0,x_1)$ be the internal label of a bead in the spring network. The actual position of this bead is specified by the vector

$$\mathbf{r}(\mathbf{x},t)=r_0(\mathbf{x},t)\epsilon_0+r_1(\mathbf{x},t)\epsilon_1$$

as shown in Fig. 1. The total potential energy stored in the springs during swelling is given in the continuum limit by

$$H=\frac{K}{2}\int d^2x\{(|\partial_0\mathbf{r}|-E)^2+(|\partial_1\mathbf{r}|-E)^2\}, \quad (1)$$

where

$$|\partial_i\mathbf{r}|\equiv[(\partial_i r_0)^2+(\partial_i r_1)^2]^{1/2}$$

is the spring length in the ϵ_i direction.

For a uniaxially growing slab, the bottom surface ($x_0=0$) is fixed and hence undeformed [i.e., $\mathbf{r}(x_0=0,x_1,t)=x_1\epsilon_1$], while the top surface ($x_0=l_0$) is free and does not support any normal or shear forces. The latter condition implies[7]

$$\partial_0 r_0(x_0=l_0,x_1,t)=E, \quad (2a)$$

$$\partial_0 r_1(x_0=l_0,x_1,t)+\partial_1 r_0(x_0=l_0,x_1,t)=0. \quad (2b)$$

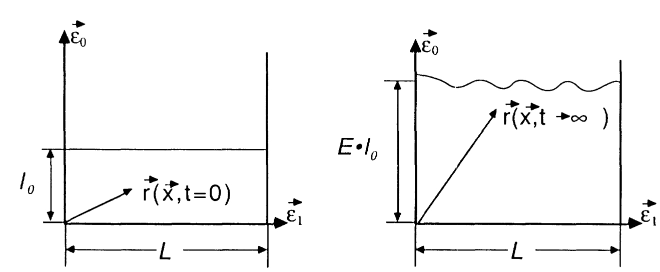

FIG. 1. A slab of gel of thickness l_0 expands uniaxially in the ϵ_0 direction; $\mathbf{r}(\mathbf{x},t)$ is the position vector of gel element $\mathbf{x}$.

As will be shown below, this zero-stress condition for the free surface provides the necessary short-wavelength stability and accounts for cusp formation. The effect of this condition is heuristically included by Tanaka *et al.*[4] in the form of a bending energy, and is anticipated by Sekimoto and Kawasaki[5] from stability considerations. The remaining boundary conditions, necessary to specify the problem completely, are that the network starts off from equilibrium, i.e., $\mathbf{r}(\mathbf{x},t \le 0) = \mathbf{x}$, and periodic boundary conditions parallel to the slab of width L, i.e., $\mathbf{r}(x_0,0,t) = \mathbf{r}(x_0,L,t)$ (and similar constraints on $\partial_i \mathbf{r}$) chosen for convenience.

In a highly viscous medium, inertial effects and kinetic energy terms can be ignored. The elastic forces are then balanced against the frictional forces, and the full motion of the beads is governed by the coupled differential equations

$$-f\partial_t r_i = \delta H\{r_0, r_1, \partial_j r_0, \partial_j r_1, \dots\}/\delta r_i.$$

These equations admit a uniformly expanding solution $r_0(\mathbf{x},t) = r_0^*(x_0,t)$, and $r_1(\mathbf{x},t) = x_1$. The expansion factor $r_0^*(x_0,t)$ satisfies a simple diffusion equation $\partial_t r_0^* = (K/f)\partial_0^2 r_0^*$, and its behavior subject to the boundary conditions specified before is depicted in Fig. 2. As the figure demonstrates, this solution is adequately approximated by two linear segments: a swollen layer of thickness $El(t)$ (i.e.,

$$r_0^*(x_0,t) = x_0 + (E-1)\{x_0 - [l_0 - l(t)]\}$$

for $x_0 > l_0 - l(t)$) on top, and an undeformed gel $[r_0^*(x_0,t) = x_0$ for $x_0 < l_0 - l(t)]$ at the bottom. The thickness of the swollen layer grows diffusively since $l(t) \sim (Dt)^{1/2}$, with $D \equiv K/f$.

The full set of coupled differential equations is too complicated to be studied *analytically or numerically*, and approximations must be made. We assume that any fluctuations on the surface layer are affinely followed by the layers below, but with reduced amplitude. We further assume that these fluctuations only exist in the swollen region, i.e., their amplitude goes to zero as $x_0 \to l_0 - l(t)$. The simplest form of $\mathbf{r}(\mathbf{x},t)$ subject to these restrictions is

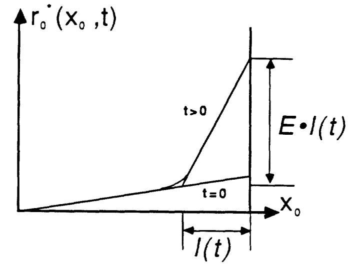

FIG. 2. Solution of the diffusion equation at time t, and its approximation by two linear segments; $El(t)$ is the thickness of the layer as measured from the surface of the gel.

$$r_0(x_0,x_1,t) = r_0^*(x_0,t) + [r_0^*(x_0,t) - x_0]w(x_1,t), \quad (3a)$$

$$r_1(x_0,x_1,t) = x_1 + [r_0^*(x_0,t) - x_0]v(x_1,t). \quad (3b)$$

This is a mean-field–type approximation as fluctuations in different vertical layers are coordinated. Note that we explicitly allow fluctuations in the lateral (ϵ_1) direction; this is a key difference between this theory and that of Tanaka *et al.*,[4] and it leads to an account of the formation of cusps as will shortly become apparent.

Using the linear approximate form for r_0^* and applying boundary condition (2b), we obtain a relation between v and w,

$$v(x_1,t) = -l(t)\partial_1 w(x_1,t). \quad (3c)$$

From Eqs. (3) we can now express H as a functional of $w(x_1,t)$ only, i.e.,

$$H = \frac{K}{2}\int d^2x [(\{(r_0^* - x_0)^2(\partial_1 w)^2 + [1 - (r_0^* - x_0) l\,\partial_1^2 w]^2\}^{1/2} - E)^2 + \{[(\partial_0 r_0^* + w\,\partial_0 r_0^* - w)^2 + (\partial_0 r_0^* - 1)^2 l^2 (\partial_1 w)^2]^{1/2} - E\}^2]. \quad (4)$$

It is worth reemphasizing that Eqs. (3) are only an approximation, and the restricted form is not exactly preserved under the full dynamic equations for $\partial_t r_i$. However, we believe that the form itself is reasonable and that the evolution of $w(x_1,t)$ can now be obtained by our varying (4) with respect to w and then averaging over the x_0 variable. To linear order in w, we get

$$\partial_t w(x_1,t) = -[D/l^2(t)]\{w + \tfrac{1}{3}(E-1)l^2(t)\partial_1^2 w + \tfrac{1}{3}l^4(t)\partial_1^4 w\}, \quad (5)$$

valid for $l^2(t) \gg 1$.

When the expansion factor is small, Eq. (5) is stable and no patterns appear. But for E larger than $E_c = 1 + 2\sqrt{3} \approx 4.464$, there is a band of unstable modes for $3 - (E-1)(lk)^2 + (lk)^4 < 0$. The stability in the short-wavelength limit is provided by the $\partial_1^4 w$ term which is a consequence of the condition of a free top surface (2b), and resembles the bending energy that was heuristically included in Ref. 3. It is clear that the unstable wavelengths (and hence the dominant wavelengths of the observed patterns) scale as $l(t) \sim (Dt)^{1/2}$. Nonlinearities obtained from the variation of $H\{w\}$ are then partly responsible for preventing the exponential growth of these instabilities. [One effect of nonlinearities is to reduce the coefficient of the $\partial_1^2 w$ term in (5) when w is large, so that the unstable band is diminished.]

Even with inclusion of nonlinearities, the function $w(x_1,t)$ does not develop any cusps (see the dashed lines in Fig. 3). However, $w(x_1,t)$ is *not* the actual surface profile, which must also include the transverse motions of the surface described by v in Eq. (3b), and required by the stress-free condition of the top surface. The actual loci of surface points is the curve $h(\xi)$ obtained with $x_0=l_0$ in Eqs. (3):

$$\begin{aligned} h(x_1,t) &= l_0+(E-1)l(t)[1+w(x_1,t)], \\ \xi(x_1,t) &= x_1-(E-1)l^2(t)\partial_1 w(x_1,t). \end{aligned} \tag{6}$$

The profiles $h(\xi,t)$ are depicted by the solid lines in Fig. 3. To see how the pattern of cusps in these profiles is generated by the smooth curves $w(x_1,t)$ (dashed lines), we examine the tangents at the surface,

$$\frac{\partial h}{\partial \xi}=\frac{\partial h}{\partial x_1}\frac{\partial x_1}{\partial \xi}=\frac{(E-1)l(t)\partial_1 w(x_1,t)}{1-(E-1)l^2(t)\partial_1^2 w}.$$

Clearly the curve $h(\xi)$ develops singularities whenever the curvature $\partial_1^2 w$ approaches $1/(E-1)l^2(t)$. This singularity occurs when the horizontal components of neighboring beads coincide, i.e., the surface becomes folded, and it signals cusp formation as illustrated in Fig. 4(a).

Once this happens, further evolution according to the original equations would have the beads go past each other, which is clearly unphysical. In fact the folded regions of the cusp are no longer part of the free surface, and evolve under a different dynamical rule. When a bead falls within the folded region, it is free to expand vertically, i.e., $\partial_1 r_0(x_0=l_0,x_1)=E$, for $x_1 \in$ (folded regions); preliminary calculations indicate that the forces trying to push the beads out of the folded region are much bigger than the forces trying to push it in. As a result, we believe that the cusp regions are all "barely folded." Our numerical recipe for implementing this effect is to evolve the beads in the folded region in such a way that $\partial_1^2 w$ is not increased. In the final stages of pattern evolution, this leads to a height-to-width ratio for a typical buckling in the cross-sectional profile that is between $\frac{1}{10}$ and $\frac{1}{4}$. The necessity for the gel surface to fold was first suggested by Onuki.[6] He assumed that *in equilibrium* there is a *finite width* over which the surface particles are in contact (i.e., folded), and calculated the final shape of buckling with this width as an unknown parameter. Our barely folded assumption corresponds to setting this width very small during pattern evolution.

This completes the prescription for following the patterns on the gel surface. Our model is completely specified by two parameters D and E which are simply related to the elastic moduli, viscosity, and the osmotic pressure of the gel. The resulting patterns in Fig. 3 (corresponding to $E=10$) reproduce various features such as scaling forms and cusps obtained in the experiments. The origin of the cusps is the following: mechanical instabilities of the swollen layer of the gel lead to height fluctuations on the surface. The height fluctuations are accompanied by transverse expansions of the surface particles which brings them in contact. At this point the particles are no longer part of the free surface and fold in cusps. Further evolution of cusps shows that these singularities can be removed by two mechanisms as indicated in Fig. 4. Either a cusp is pushed out by neighboring regions [Fig. 4(b)], or two neighboring cusps merge to form a single one [Fig. 4(c)]. The equilibrium profiles obtained are in qualitative agreement with observations.

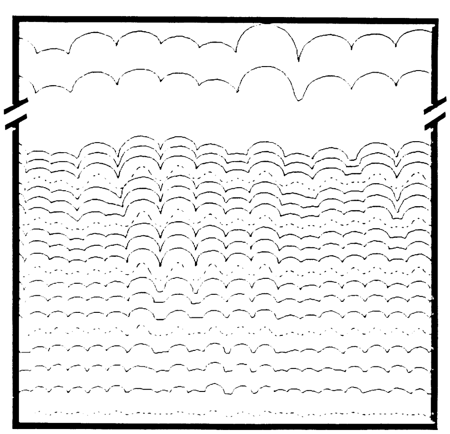

FIG. 3. The *nonlinear* equation of motion for $w(x_1,t)$ obtained from variation of (4) is solved numerically (for $E=10$) at various stages of evolution: The dashed lines, $h(x_1,t)$, are profiles obtained when no horizontal displacement is allowed; the solid lines, $h(\xi,t)$, are the surface profiles when the horizontal motion is included.

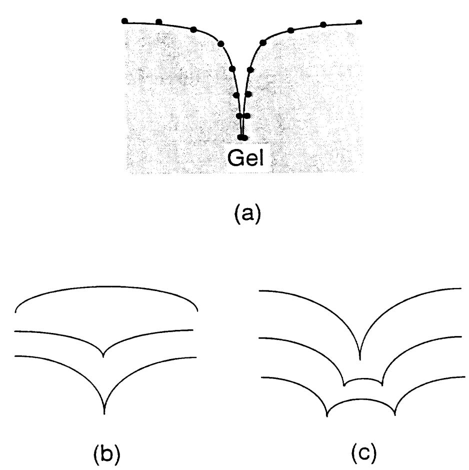

FIG. 4. (a) Cusps are formed when beads from the surfaces of neighboring arcs run into each other. (b),(c) Two mechanisms for the merging of cusps, as found from computer simulations.

A real gel is actually highly cross linked at random; a more realistic model would have (weaker) springs connecting the diagonals of the square lattice, thus requiring two independent elastic moduli as is expected by symmetry considerations alone. The addition complicates[7] boundary condition (2a), and the uniformly expanding solution will have an E_{eff} which is a function of E and the ratio of the two elastic constants. The new Hamiltonian also results in small changes in the coefficients of the $\partial_1^2 w$ and $\partial_1^4 w$ terms in (5), but should not change the characteristic behaviors of the solution. The reason is that in $1+1$ dimensions, upon the reduction of the problem to that of a free string, the additional shear energy can only add to the string's stretching and bending energies which are already present in (1); only one elastic constant is needed to describe a string.

Finally, we can extend our model to $2+1$ dimensions by generalizing the Hamiltonian in (1) to including an additional transverse direction ϵ_2. However, in this case, the diagonal springs do become necessary, because when we try to reduce the problem down to that of a free membrane, two elastic constants are now needed to describe its dynamics, even though the presence of diagonal springs in planes perpendicular to the surface still adds nothing new. Despite this difference, we believe that the characteristics of the cross-section profiles found in $1+1$ dimensions are preserved; and indeed a simulation of the 2D version of the *linear growth equation* (5) resulted in formation of honeycomblike networks by cusps, in agreement with observed patterns.

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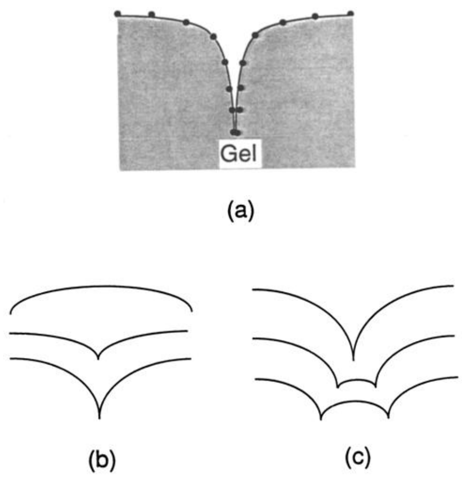

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