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Surface-pattern evolution in a swelling gel under a geometrical constraint: Direct observation of fold structure and its coarsening dynamics

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We demonstrate here the direct observation of the side view of surface folds in a swelling gel, which are induced by elastic instability. The fold structure along the thickness direction has been clarified, which is a prerequisite for understanding its singular nature. The elementary coarsening process of the fold pattern is a discrete process and no transverse motion of folds along the surface direction is observed. The fold pattern grows self-similarly; however, the shape characteristics of the fold pattern are dependent on the initial thickness of the gel. This indicates that the shape of the fold is dependent on the strength of the constraint from the bottom surface.

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It is well known that a free surface of an elastically stressed body is unstable if elastic [1] or diffusional [2,3] deformation is allowed. This phenomenon has been widely known for elastic solids including polymer films, metals, and semiconductors. The similar surface instability and the resulting pattern evolution have recently been found by Tanaka and co-workers [4,5] also for gels undergoing volume phase transition [6–9]. Since then the surface-pattern formation of a gel has been extensively studied from both the experimental [4,5,10,11] and the theoretical viewpoints [12–14]. Instability which causes the pattern evolution in gels is likely originated from the mechanical constraints including both internal and external origins. Since both shrinking and swelling of gels are governed by a diffusion process, swelling or shrinking gels intrinsically have spatial inhomogeneity, which induces mechanical instability. There is no way that a whole gel homogeneously changes its volume. If there is no geometrical constraint to a gel, the pattern should be transient and gradually disappear as the gel becomes homogeneous again. On the other hand, a geometrical constraint to a gel produces inhomogeneous stress fields inside the gel and could cause an infinitely stable pattern. The similarity of stress-induced surface instability between gels and elastic solids has been pointed out from the theoretical viewpoints [12,14]. The singular nature of the fold structure has made the understanding of this phenomenon beyond the linear stability analysis very difficult.

A gel is one of the most suitable model systems to study the surface instability of an elastically stressed body since the pattern is macroscopic, which makes the experimental study very easy. The most typical stable pattern caused by volume phase transition is the surface pattern of a swelling gel, whose lower surface is clamped to a flat plate and whose upper surface is free and in contact with solvent. In this configuration, the gel is allowed to swell uniaxially. The zero-stress condition on a free surface leads to short-wavelength stability and causes cusp formation. Recently two-dimensional (2D) patterns on the surface of a swelling gel slab in this configuration have been extensively studied [4,5,11]. This type of study on 2D patterns gives us a hint at understanding this strongly nonlinear problem. However, the 2D projection of the pattern is not enough to understand the strongly singular nature of the cusp since it grows along the thickness direction. For its deeper understanding, thus, it is a prerequisite to know 3D information such as fold depth and cusp shape. Unfortunately, all the experimental studies on the surface pattern including gels have so far been limited to 2D surface patterns, i.e., the top views of surface patterns. In this paper, we demonstrate a direct observation of the side views of fold structures in gels.

Gels were prepared by the same method as in Refs. [4,5,11]. A copolymer of acrylamide (AA) with sodium acrylate (SA), crosslinked by N,N'-methylenebisacrylamide (BISAA), was synthesized by using free radical polymerization, initiated by ammonium persulfate and catalyzed with N,N,N',N'-tetramethylenediamine. The ratio AA:SA:BISAA was fixed to 5:2:0.2. This gelation process was performed in a thin cell which was composed of the two flat glass plates of 25×7 cm^2 with spacer glasses of 1 mm thickness. The bottom of the cell was sealed by a so-called gel bond film. Thus the gel was sandwiched by two glass plates with a gap of 1 mm and its bottom surface was covalently crosslinked and clamped to the gel bond film. This configuration enables us to observe the side view of a gel slab during its swelling process. The water was colored by blue ink to see the gel surface clearly. The time when we put the colored water into the cell was the initiation of the swelling process. The elapsing time t was measured from this time. The patterns were quantitatively analyzed by digital image analysis (DIA) [15].

Here we show experimental results on two gels with different initial thicknesses h_0 of 2.9 and 9.4 mm. Figures 1(a) and 1(b) indicate the temporal change of fold patterns. The fold pattern was extracted by a two-valuation (black and white) operation. In both cases, initial small fluctuations enhance with time and form sharp folds. Then the fold depth monotonically increases with time. We can clearly see an increase in the total gel volume with time. The most striking feature is that there is no motion of folds along the x axis. The number of sharp folds monotonically decreases with time.

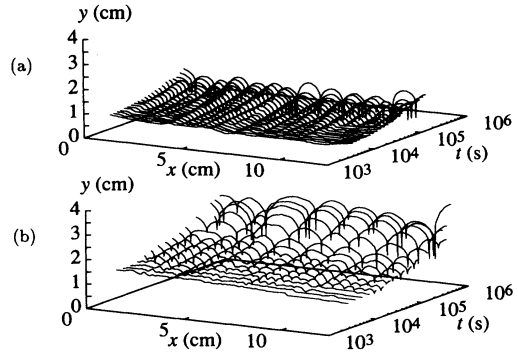

FIG. 1. Temporal change in the fold pattern, or surface height function $h(x)$. (a) $h_0 = 2.9$ mm and (b) $h_0 = 9.4$ mm.

Figure 2 shows the temporal change in the Fourier power spectrum of the surface height function $h(x)$ indicated in Fig. 1(a). The power spectrum has many peaks and there is no smooth, continuous change in the peak position, which supports the discrete feature of the fold annihilation. The higher order peaks increase their intensities with t, indicating the strong nonlinear (singular) nature of the fold patterns. Figure 3 indicates the temporal change in the typical peak wave numbers of the power spectrum. Here we can also see the discrete feature. The averaged characteristic wave number k_p grows as $t^{-1/2}$ irrespective of the initial thickness h_0, which is consistent with our previous results on 2D gels [11]. Figure 4 shows the temporal change in the average height increase of the gel, Δh ($\Delta h = h_{\mathrm{av}} - h_0, h_{\mathrm{av}}$: the average height of the gel), which is proportional to volume expansion. It is found that $\Delta h \propto t^{1/2}$ irrespective of h_0. Since both k_p^{-1} and Δh have $t^{1/2}$ dependence, the swelling gels are in the diffusion regime, namely, in the weak constraint regime [11].

Figures 5(a)–5(c) show the temporal change in the three important quantities characterizing the shape of the fold pattern, $\langle L_\perp \rangle$, $\langle L_\parallel \rangle$, and $\langle L_\parallel \rangle / \langle L_\perp \rangle$. $\langle L_\perp \rangle$ is the average interfold distance, and $\langle L_\parallel \rangle$ is the average amplitude of the surface undulation. The definitions of these quantities are indicated in Fig. 5(a). Both $\langle L_\perp \rangle$ and $\langle L_\parallel \rangle$ grow with time as $t^{1/2}$, although they start to deviate from $t^{1/2}$ dependence in the late stage. The ratio $\langle L_\parallel \rangle / \langle L_\perp \rangle$ is almost constant with time, strongly indicating the self-similarity of the fold pattern. However, it should be noted that $\langle L_\parallel \rangle / \langle L_\perp \rangle$ is dependent on the initial gel thickness h_0. Figure 6 shows the temporal change in the fold depth L_{fold}. Some folds grow monotonically with time, while the others disappear. Here we analyze only the depth of a growing fold. The relation $L_{\mathrm{fold}} \propto t^{1/2}$ is obtained (see Fig. 6). Thus L_{fold} is proportional to the diffusion length, i.e., the thickness of the swollen gel layer. The ratio $\langle L_\parallel \rangle / L_{\mathrm{fold}}$ which is constant with time is about the same for different values of h_0. This indicates that both $\langle L_\parallel \rangle$ and L_{fold} depend on h_0 in the same way.

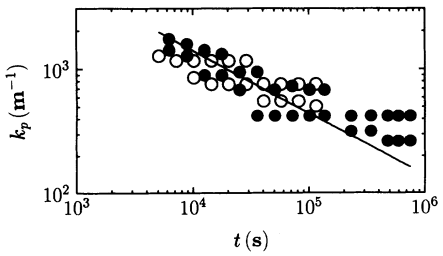

FIG. 3. Temporal change in typical peak wave numbers (k_p) of the power spectrum. Solid line has a slope of $-1/2$. Open circle: $h_0 = 2.9$ mm; filled circle: $h_0 = 9.4$ mm.

Figure 7 shows the breaking process of the gel ($h_0 = 2.9$ mm), which was commonly observed for any gel with 1+1 dimensions when a fold line approached the bottom surface.

First we discuss the overall growth behavior. The swollen part of a gel increases with time by diffusion. This causes the mechanical instability and leads to the surface undulation. By further increase in the swollen part, the surface undulation enters into a nonlinear regime and forms the cusps into the gel. This diffusion process is so slow that the pattern can be regarded in the quasiequilibrium state. Thus we can argue the pattern evolution on the basis of (i) a 1D diffusion equation and (ii) the assumption that the fold period is proportional to the diffusion length, which is the only relevant length scale in the system. The result that both k_p^{-1} and Δh grow as $t^{1/2}$ supports this diffusion model [4,11]. The fact that the behavior is independent of h_0 also supports this model. The present study in a 1D gel is always restricted to the diffusive growth regime since the gel breaks just before entering the relaxational regime where diffusion gradually stops because of the finiteness of the gel thickness.

Next we consider the fold formation and the coarsening dynamics. The geometrical constraint to a swelling gel leads to its mechanical instability, which causes surface corrugations. Growing corrugations touch each other,

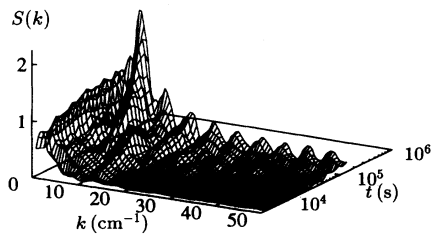

FIG. 2. Temporal change in the Fourier power spectrum [$S(k)$] of surface height function $h(x)$ for the gel with $h_0 = 2.9$ mm.

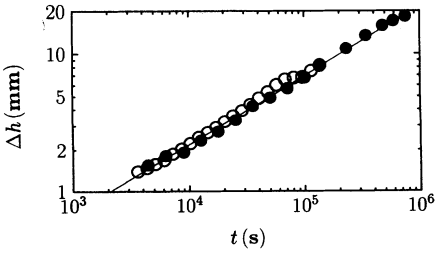

FIG. 4. Temporal change in the average height increase of the gel (Δh). Open circle: $h_0 = 2.9$ mm; filled circle: $h_0 = 9.4$ mm. Solid line has a slope of 1/2.

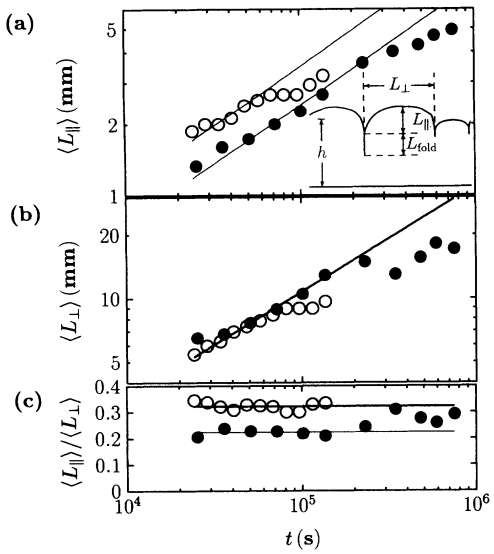

FIG. 5. Temporal change in $\langle L_\parallel \rangle$ (a), $\langle L_\perp \rangle$ (b), and $\langle L_\parallel \rangle / \langle L_\perp \rangle$ (c). Open circle: $h_0 = 2.9$ mm; filled circle: $h_0 = 9.4$ mm. Solid lines in (a) and (b) have a slope of 1/2. Solid lines in (c) have a slope of 0. The small figure in (a) schematically explains the definitions of $\langle L_\parallel \rangle$, $\langle L_\perp \rangle$, and $L_{\rm fold}$.

then form cusps into gel, and eventually form the folded parts (see Fig. 1). This is because the volume expansion accompanies the transverse expansion of the swollen layer which makes the surface in contact because of the geometrical constraint. After formation of a fold or cusplike structure, there is no translational motion of the fold along the x axis (as seen in Fig. 1). This indicates that there is a large energy barrier for the translational fold motion. The motion of the fold accompanies the additional compression of the gel; it might even require the destruction of a gel network structure or the complete reorganization of a fold structure. This difficulty of the fold motion originates from the topological characteristics of a gel network: the interconnectivity of a network structure or the impenetrable nature of a gel. Thus, once a singular cusp is formed, the fold motion in a lateral direction is no longer allowed even when there is an imbalance in the side pressures at the folded region. Similar behavior is observed in the numerical simulation by Hwa and Karder [13]. This tendency might be stronger for a 1D pattern than for a 2D pattern because of the lesser degree of freedom of motion for the former. Thus the initial

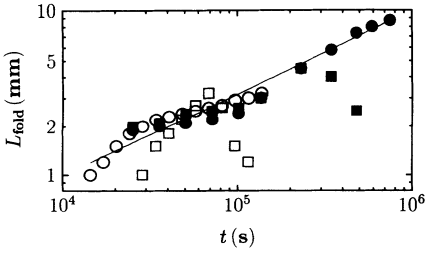

FIG. 6. Temporal change in $L_{\rm fold}$. Circles: growing folds; squares: disappearing folds. Open symbols: $h_0 = 2.9$ mm; filled symbols: $h_0 = 9.4$ mm. Solid line has a slope of 1/2.

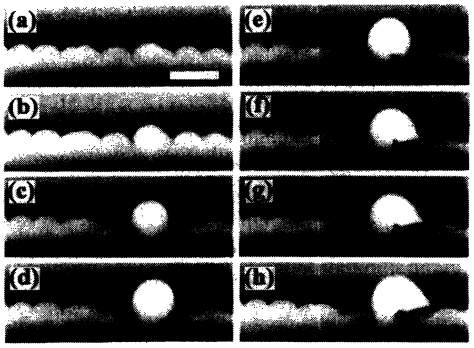

FIG. 7. Destruction of the gel and the resulting relaxation process of the internal stress stored due to the geometrical constraint. The gel has an initial thickness of 5 mm. (a) corresponds to t_a = 449 160 s. (b)–(h) correspond to 420 s, 480 s, 600 s, 720 s, 780 s, 1560 s, and 13 200 s from t_a, respectively. The bar is 20mm in length.

configuration of cusps dominates the entire history of the pattern evolution; in other words, a gel can never reach the lowest energy state at least in the diffusion regime and is likely trapped in a local equilibrium state having a memory of the initial pattern. This is a very important characteristic of the fold pattern evolution. The coarsening process of a fold pattern is dominated by the gradual disappearance of folds as in Fig. 1. This process is a result of the gradual volume expansion caused by diffusion. The most natural way for a gel to expand further after the formation of cusps is the expansion of cusp regions towards the outside of the gel, which leads to the disappearance of folds. The diffusion is a continuous process, but the resulting coarsening dynamics is a discrete process because of the singular nature of cusps.

The elastic interaction among the folded lines is produced through the 3D nature of the deformation. When one fold disappears, this leads to the imbalance of the lateral pressure at the neighboring folded regions, which likely accelerates the disappearance of the second-nearest-neighbor folds of the disappeared one; thus, there is probably a transverse interaction between folds.

Some folds increase their depths with time and finally reach the bottom. This process is also described by $t^{1/2}$ behavior as shown in Fig. 6. Once a fold considerably approaches the bottom surface, the gel becomes very difficult to expand further and the fold pattern likely enters in the final relaxational regime. Unfortunately this regime could not be observed in a 1D gel since the fold structure is broken when the fold line approaches the bottom (see Fig. 7). This is likely because the stress overcomes the bonding strength. From the quick, enormous expansion of the broken gel (see Fig. 7) we can learn how strongly a gel is compressed in the transverse direction by the mechanical constraint from the bottom. For a 2D gel, on the other hand, the bonding strength is likely strong enough to support the stress stored in the gel probably because the ratio between the folded part and the bonding area is much smaller for a 2D gel than for a 1D gel. Actually we have rarely observed such behavior in a 2D gel undergoing the volume expansion transition (see Ref. [11]).

Finally we discuss the shape characteristics of the fold pattern. The three characteristic lengths, $\langle L_\perp \rangle$, $\langle L_\parallel \rangle$, and $L_{\rm fold}$, are found to have the same time dependence of $t^{1/2}$ (see Figs. 5 and 6); thus, $\langle L_\parallel \rangle / \langle L_\perp \rangle$ and $\langle L_\perp \rangle / L_{\rm fold}$ are both constant with time. This means that the geometrical characteristics of the pattern do not change in time; in other words, *the fold pattern grows self-similarly.* However, the pattern is not universal because of the different dependences of the characteristic lengths on h_0: The characteristic length perpendicular to the thickness direction, $\langle L_\perp \rangle$, is independent of h_0, while the characteristic lengths along the thickness direction, $\langle L_\parallel \rangle$ and $L_{\rm fold}$, are dependent on h_0. This behavior can be qualitatively explained as follows: The strength of the mechanical constraint is dependent on the vertical size of the gel. For a thicker gel, the mechanical constraint from the bottom can be relaxed in a larger degree and is weaker than for a thinner gel because of the thicker unswollen layer of gel for the former. The unswollen layer can bear part of the stress. Thus the shape of the fold pattern depends on h_0. The strength of the constraint is probably a function of the initial gel thickness h_0 and the network density [16]. Further experimental and theoretical studies are necessary for a quantitative understanding of the growth behavior of $\langle L_\parallel \rangle$ and $L_{\rm fold}$, especially their dependences on h_0.

In summary, we have succeeded in observing the side view of a gel undergoing volume phase transition and in studying the cusp formation dynamics and the coarsening dynamics of the fold pattern. The singular structure of the fold is directly observed. The fold is found to be barely folded and the width of the folded region is extremely narrow. During coarsening of the folded pattern, no translational motion of folds has been observed, indicating that there is an extremely large energy barrier for the lateral motion of folds. This results in a unique coarsening process such that the folds disappear one by one. This discrete process can also be recognized in the temporal change in the structure factor. The fold pattern is found to grow self-similarly; however, it is not universal in the sense that the shape is dependent on the initial thickness of the gel. The destruction of the gel has also been found when a fold line reaches the bottom. These experimental results in 1+1 dimensions can be directly compared with numerical simulations and analytical theories in the same configuration [12–14]. We hope that the present study will give a strong hint at a deep understanding of the evolution of strongly singular patterns which are commonly observed for an elastically stressed body.

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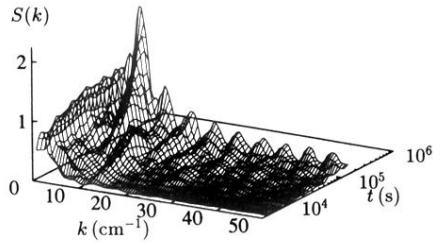

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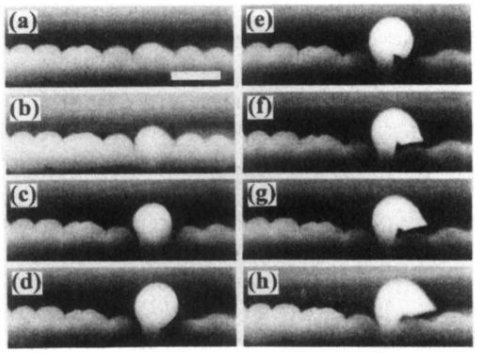

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