Mechanical Instabilities of Gels

Julien Dervaux and Martine Ben Amar

Département de Physique, Laboratoire de Physique Statistique de l’Ecole Normale Supérieure (UMR 8550), associé aux Universités Paris 6 et Paris 7 et au CNRS; 75005 Paris, France; email: benamar@lps.ens.fr

Abstract

Although the study of gels undoubtedly takes its roots within the field of physicochemistry, the interest in gels has flourished and they have progressively become an important object in the study of the mechanics of polymeric materials and volumetric growth, raising some fascinating problems, some of them remaining unsolved. Because gels are multiphase objects, their study represents an important step in the understanding of the mechanics of complex soft matter as well as for the process of shape generation in biological bodies. The scope of this article is to review the understanding we have of the mechanical behavior of gels, with a strong focus on the development of instabilities in swelling gels.

Keywords

buckling, creasing, biological growth, morphogenesis, phase transition, nonlinear elasticity
1. INTRODUCTION

A gel is a liquid trapped within a diluted mesh of cross-linked polymer chains. The systematic study of gels, started in the 1940s, takes undoubtedly its roots within the field of physicochemistry. Indeed, as a result of the complex interactions between the polymer chains and the solvent molecules, gels exhibit a volume phase transition during which they may absorb several thousand times their own weight in solvent in response to a tiny change in environmental conditions. Consequently, gels had initially been a subject of choice for the development of the theory of phase transitions, along with polymer chains and solutions.

As we see throughout this review, however, thanks to fascinating studies from the 1970s and the following two decades, the interest in gels has flourished and they have progressively become an important object in the study of the mechanics of polymeric materials and volumetric growth. Well known to physicists, a growth process opens the door to the possibility of self-organization and the emergence of spatiotemporal patterns. Indeed, because the association of a solvent with a polymer network exhibits a rather complex mechanical behavior, sharing properties of both liquids and solids, unique features were observed during the swelling process of gels thanks to, among others, the pioneering work of Toyoichi Tanaka.

But, why write a review on pattern formation in swelling gels now? Despite the considerable amount of work performed until the 1990s, some problems, such as the formation of the creasing instability, one of the hallmarks of gel swelling, have not been fully understood. Recently, however, highly controlled experiments have brought new results, shining light on pattern formation in swelling gels and allowing for detailed comparisons with theoretical and numerical models. Furthermore, there is an increasing interest in the physics community in the behavior of biological objects, which are undoubtedly the ultimate example of complex soft matter. Interestingly, many growing biological objects possess a gel-like structure, and recent advances in developmental biology require the development of sophisticated models able to describe the concurrent mass production and reorganization processes that enable the reproducible generation of shapes in living objects. Although growing and swelling are obviously distinct processes, the fundamental understanding of mass reorganization in swelling gels provides important tools to describe the more complex processes involved during biological growth.

As such, gels represent an important step in the understanding of the mechanics of complex soft matter and lie at a crossroad of interests between several scientific communities. The scope of this article is to review the understanding we have of the mechanical behavior of gels, with a strong focus on recent developments concerning swelling-induced instabilities in gels as well as its connection with problems of biological growth.

2. POLYMER NETWORK

Before introducing some important properties of the gel network, let us briefly mention a few simple but useful concepts developed in the theory of polymer solutions.

2.1. Polymer Chains and Solutions

Let us start with a simple problem beginning in the 1930s and consider a single polymer chain, made of N monomers immersed in a solvent. What is, in a statistical sense, the configuration of this chain? From the pioneering works of Huggins and Flory (1–3), we learn that, in the thermodynamic limit, the macroscopic state of the chain must be a minimum of its Gibbs free energy, which encapsulates two contributions of distinct physical origins. The polymer-solvent
interactions as well as the intramolecular interactions of the monomer subunits between themselves are described by the enthalpy of mixing. The strength of those interactions depends on the temperature. In a good solvent, it is favorable for the monomer units to be surrounded by solvent molecules, whereas a polymer chain in a bad solvent tends to maximize the monomer-monomer interactions. In the absence of thermal activity one would therefore expect to observe either completely straight or collapsed chains. Because of thermal motions, however, such states are not observed because they can only be attained by a very small number of configurations of the chain and hence, states of low entropy. Rather, thermal activity drives the chain toward states of higher entropy. This is the second contribution to the Gibbs free energy.

The balance between the enthalpy and entropy of mixing therefore selects the state of a polymer chain. More quantitatively, the state of a chain can be intuitively described by the radius $R$ of the characteristic volume it occupies. Of course, the longer the chain, the larger the volume, and the radius $R$ must be an increasing function of the number $N$ of monomer subunits. Scaling laws of the form $R \propto N^v$ are both simple and useful tools to characterize the state of a chain (4). In a bad solvent, the chain contracts and occupies a very small volume with $v = 1/3$. In this so-called globule state, the chain is highly condensed, and the volume $R^3$ occupied by the chain scales as the number $N$ of its constituent, as if it were a solid compact material. In a good solvent, however, the situation is markedly different, and the chain tends to occupy a much larger volume with a critical exponent of $v \approx 3/5$. This is the coil state.

The phase transition from the globule to the coil state can be triggered by changing the quality or temperature of the solvent, for example. Using Laudau’s terminology, this phase transition can be either first or second order, meaning that an infinitesimal change in external conditions can yield (respectively) a finite or infinitesimal change in the chain size, depending on the stiffness of the polymer (4, 5). During this transition, the critical exponent $v$ changes and at some point reaches the value $v = 1/2$. This point, which is reached at a specific temperature for a given solvent, is a major concept in polymer theory and is known as the $\Theta$-point. A critical exponent of exactly one-half is the signature that the polymer chain behaves exactly as an ideal Gaussian chain. In practice, excluded volume effects render such a random walk physically unrealistic, because real chains cannot self-intersect. Instead, the physical interpretation of the $\Theta$-point is that the intermolecular interactions exactly cancel the excluded volume effects. Because the chain behaves ideally at the $\Theta$-point, it is possible to measure precisely various microscopic properties of the chain, independently of the solvent quality, such as the bond angle formed between adjacent monomers.

Although the coil-globule transition, first predicted by Stockmayer (6) in 1960, had been extensively studied theoretically (7–10), it was first observed experimentally on a single chain of polyacrylamide by Toyoichi Tanaka and colleagues in 1979 (11). In a polymer solution, this coil-globule transition is manifested by a phase separation of a homogeneous mixture into distinct domains of different composition. In some cases, in domains of high polymer concentration, the mobility of the chains may drop drastically, turning the polymer domains into glassy amorphous solids. This glass transition occurs below a critical temperature. As an example, the glass transition temperature of acrylamide, a polymer frequently used in various experiments, is $T_g = 165^\circ$C.

2.2. Gels

Polymeric gels have much in common with polymer solutions. However, they are characterized by an additional property: Their polymer chains are cross-linked and form a network. This difference has an important consequence as it endows the solvent-polymer mixture with
memory and resilience. Consequently, the behavior of gels is somewhere between those of solids and liquids. In a fashion similar to that of a single chain or a polymer solution, polymer chains within a gel retain the ability to undergo a coil-globule transition. In opposition with a polymer solution, however, a network of cross-linked polymer chains does not dissolve in a good solvent. Rather, the network expands until the elasticity of the chains counteracts the expansive forces that drive the polymer chains away from each other. In a poor solvent, the gel collapses, possibly turning into a brittle glass, depending on the composition and temperature of the gel. The volume phase transition of the gel is a process known as swelling (12, 13). Because some energy can be stored elastically within the gel, modifications were made to the Flory-Huggins free energy of polymer solutions (14–16). However, a gel is far from being a purely elastic body either. Indeed, when a sample of gel is compressed, it releases some solvent and thereby dissipates some energy viscously.

In the footsteps of the studies on the coil-globule transition, much work has been done to characterize the transition from a swollen to a shrunken phase in gels. Tanaka conducted experiments by immersing small samples of polyacrylamide gels in an acetone-water mixture. When the concentration of acetone, a bad solvent for acrylamide, is lowered, the gel swells. Interestingly it was found that the swelling transition of freshly prepared gels was a second-order transition with a continuous increase in volume for decreasing acetone concentration, whereas older gels would undergo a first-order transition characterized by a discontinuous change in volume at a critical acetone concentration. Furthermore, the volume variation was much more important for older gels. This puzzling observation was later shown to be a consequence of the hydrolysis that took place during the storage of gels that were placed in an alkaline environment (17). The ionization of the gel network has a dual effect: (a) The presence of charges along the polymer chains increases the electrostatic repulsion of the chains with themselves, thereby favoring straight configuration of the chains. (b) Furthermore, because counterions are bound to stay within the gel for electroneutrality reasons, they create an additional osmotic pressure that motivates the solvent molecules to enter the gel. Together those effects were theoretically found to lead to both a discontinuous and much larger [up to 20 times larger (18)] volume transition.

Besides solvent quality, many factors can trigger this phase transition, such as pH (19), light (20), temperature (21), electric field (22), ionic strength (17), or various biological compounds (23). Gels made of natural polymers also exhibit a swelling transition (24). Depending on the nature of the solvent and polymer, the swelling transition can be first or second order. Some attention has also been given to the coexistence of different phases (25, 26). In particular, the boundary between different phases was found to be macroscopic (Figure 1), in opposition with many other phase transitions. This was later proven to be a consequence of the elasticity of the network (26).

Depending on the chemical composition of the gel as well as the polymerization protocol, gels with markedly different architectures and porosities can be produced. In particular, the mesh size of the network affects the transport mechanism (diffusion, convection, or both) of the solvent molecules within the network.

### 3. SWELLING KINETICS

Once the properties of a gel at the thermodynamic equilibrium were at least partly understood, the next natural task was to understand the path taken by a gel to reach this thermodynamic equilibrium. Consequently, researchers started to focus on the kinetics of the swelling process. In many cases, the phase transition is initiated locally and a swelling (or drying) front propagates
within the sample until the final state is reached. In such a situation, the geometry of the sample is of paramount importance, obviously. Using light scattering techniques, Tanaka and coworkers found in 1973 that the motion of the polymer network itself was diffusive, despite the fact that polymer chains were cross-linked (16, 27). For this reason, the term collective diffusion was coined to describe the motion of the polymer network. Another classical example, also investigated by Tanaka & Fillmore shortly thereafter, concerns spherical beads of gels transferred from a bad solvent to a good solvent (28). Because only the surface of the sphere is in contact with the good solvent, the swelling process is strongly inhomogeneous. Experiments conducted on 5% polyacrylamide gel beads have revealed that the characteristic time of the swelling process is proportional to the square of the radius of the bead, indicating a common diffusive process (obeying Fick’s law).

3.1. The Collective Diffusion Model

On the basis of the previous observations, Tanaka, Hocker & Benedek (THB) (27) and Tanaka & Fillmore (28) developed a kinetic theory for the swelling of gels. Assuming that the solvent was at rest, they wrote an equation of motion for the polymer network. We briefly summarize here the outline of the collective diffusion model. Let us consider a one-dimensional network and denote by \( u \) the displacement of the network from its reference position \( X \). Under the assumption that the network behaves as an ideal linear spring, the stress \( \sigma \) is related to the strain \( \epsilon \) through Hook’s constitutive law:

\[
\sigma = K \epsilon = K \frac{\partial u}{\partial X},
\]

where \( K \) is the longitudinal elastic modulus. In the collective diffusion model, the central idea is that the displacement of the gel network is impeded by the friction with the solvent, resulting in a viscous drag. Therefore the following evolution equation for the gel network was suggested:

\[
\frac{\rho \partial^2 u}{\partial t^2} = \frac{\partial \sigma}{\partial X} - f \frac{\partial u}{\partial t} = \frac{\rho \partial^2 u}{\partial X^2} - f \frac{\partial u}{\partial t},
\]

where \( \rho \) is the density of the gel network, \( f \) is the frictional force, and \( \rho \) is the mass density.

---

**Stress**: force per unit area; depending on whether the force is tangential or normal to the surface, it is further specified as a shear or a normal stress, respectively.

**Strain**: dimensionless measure of a deformation, which can be decomposed into an angle-preserving component (the compressive strain) and one that quantifies the amount of distortion of angles (the shear strain).

**Elastic modulus**: a material constant; the longitudinal (respectively shear) elastic modulus is defined as the ratio of compressive (respectively shear) stress over compressive (respectively shear) strain.
which is nothing but a damped wave equation. In the overdamped regime of interest, it is reasonable to neglect the inertial term, yielding the following collective diffusion equation:

\[
\frac{\partial u}{\partial t} = -\frac{K}{f} \frac{\partial^2 u}{\partial x^2},
\]

where the ratio \( D_{\text{coll}} \equiv K/f \) is interpreted as the collective diffusion coefficient. In this simple account of the collective diffusion model, the transverse motions are neglected so that no couplings between the different directions are incorporated in this framework. Furthermore, the effect of shear has been neglected so that only the longitudinal elastic modulus enters in the previous equations. Although the first approximation is essentially valid for specific geometries such as spheres, long cylinders, or large discs (29), the assumption of negligible shear was later recognized to be in general incorrect (29–32). In particular, the existence of a nonzero shear modulus affects the effective collective diffusion coefficient \( D_{\text{coll}} \), which was found to be smaller for cylinders and discs than for spheres. The relative values of \( D_{\text{coll}} \) for spheres, cylinders, and discs were 1, 2/3, and 1/3, respectively (30). The argument put forward by Tanaka to explain this result is the following. In the spherical geometry, diffusion occurs in three dimensions. In a cylinder with a high length/diameter aspect ratio, it is reasonable to assume that diffusion occurs only radially. Until the solvent reaches the axis of the cylinder, there exists a cylinder of shrunken gel surrounded by a tube of swollen gel. Because of shear, the central part prevents the cylinder from expanding axially, and diffusion is said to occur only in two dimensions (radially and circumferentially). Once the solvent permeates the central part, the gel suddenly relaxes and expands axially. The volume gained by the two-dimensional diffusion process must thus be shared with the third (axial) dimension. In a disc of finite thickness and infinite radius, diffusion only occurs in the axial dimension and not in the plane of the disc. When the solvent reaches the middle plane of the disc, it suddenly expands and the increase in thickness must be shared by the two remaining dimensions. The reduction in the diffusion coefficient is a consequence of the diffusion occurring only in a limited number of directions (3, 2, and 1 for spheres, cylinders, and discs), the increase in volume being then shared, through a shear relaxation process, with the remaining dimensions. Accordingly, this argument yields relative values of \( D_{\text{coll}} \) of 3/3, 2/3, and 1/3, respectively for spheres, cylinders, and discs, in good agreement with the experimental determination (30).

### 3.2. The Effect of Fluid Flow

Despite its simplicity, the collective diffusion model could explain reasonably well the first experimental results on the kinetics of swelling gels, and in particular the diffusive behavior of the cross-linked polymer network. However, it was soon recognized that all features could not be reproduced (30, 33–38). The main limitation of this model stems from the assumption of negligible fluid displacement. Consequently, it is not possible to analyze correctly, for example, problems involving fluid flows at their boundary, as highlighted by References 35–37 and 39, which investigate the evolution of a gel compressed by a permeable piston. Furthermore, because the momentum transfer between the two phases is neglected, the gel cannot deform instantaneously in response to an applied load (40, 41). Indeed, on a very short timescale following the sudden compression of the gel sample, the solvent molecules do not have time to diffuse. Consequently, a hydrostatic pressure builds up within the liquid phase and contributes to the total stress in the gel, an effect neglected within the framework of the collective diffusion model.
Additionally, the permeation process is not always governed solely by diffusion, and experiments have been reported in which the characteristic time of the swelling process does not scale like the square of the typical length scale of the sample (see, e.g., References 42 and 43). Such behavior is observed when the mobility of the polymer chains is extremely poor, such that the characteristic time of relaxation of the chains exceeds that of diffusion. This is typically the case when a gel in a glassy state is brought in contact with a solvent. A very sharp front, propagating at a constant velocity, is observed. In this situation, diffusion is Fickian in the swollen region behind the front, while the permeation process at the front is governed by the relaxation of the polymer network. This transport mechanism is usually referred to as case II diffusion. In between Fickian and case II diffusion, when the characteristic timescale for diffusion and polymer relaxation is of the same order, an intermediate behavior, called anomalous diffusion, is observed. On the other end of the spectrum, one finds superporous gels (44). Such gels have pores with typical diameters of 0.1 μm, and the swelling process is driven mostly by capillary forces rather than diffusion. The swelling kinetics of such gels is extremely fast and independent of the size of the gel.

Consequently, because the fluid is omitted, it is difficult to generalize this simple model to cases where the diffusion of the solvent particles becomes more complex. To account for the effect of fluid flows, refinements to this model have been attempted (45–47). Despite this limitation and some inconsistencies, the collective diffusion model and its subsequent modifications, developed in the seventies and eighties, have been almost exclusively used to analyze the swelling of gels. It was only recently recognized that the collective diffusion model, when correctly extended to take fluid flow into account (34), is equivalent to the linear theory initially written by Biot in 1941 in the context of poroelasticity (39, 48) and the closely related framework of mixture theory (49).

### 3.3. Linear Poroelasticity

The general idea is to recognize that, in fact, the stress in the gel has two contributions, one part arising from the elastic phase of the gel (the polymer network) and one arising from the fluid phase. Therefore Equation 1 must be understood as the constitutive equation for the solid stress \( \sigma^S \) only. In addition, the viscous force arises only when the solvent and the network move relative to each other. Writing \( v \) for the velocity of the fluid phase, the balance of linear momentum for the solid phase becomes

\[
\mathbf{f} \left( \frac{\partial \mathbf{u}}{\partial t} - \mathbf{v} \right) = \frac{\partial \sigma^S}{\partial X}.
\]

There must be a similar balance law for the fluid phase. Denoting \( \sigma^F \) as the stress in the fluid and by virtue of Newton’s third law, we may write

\[
-\mathbf{f} \left( \frac{\partial \mathbf{u}}{\partial t} - \mathbf{v} \right) = \frac{\partial \sigma^F}{\partial X}.
\]

Under the assumption that the stress in the fluid is purely hydrostatic, i.e., the viscosity of the fluid is only relevant at the pore scale, \( \sigma^F = -\rho \) and the last equation becomes Darcy’s law. Adding Equations 4 and 5, we get the balance of linear momentum for the gel as a whole: \( \partial(\sigma^S + \sigma^F)/\partial X = \partial(\sigma)/\partial X = 0 \). Together with the continuity equation, the evolution of the gel is described, in this simplified one-dimensional framework, by

\[
\frac{\partial}{\partial X} \left( D \epsilon \frac{\partial \epsilon}{\partial X} \right) = \frac{\partial \epsilon}{\partial t}, \quad \frac{\partial \sigma}{\partial X} = 0 \quad \text{and} \quad \sigma = K \epsilon - \rho.
\]
Within this framework, it is much easier to describe more complex diffusion processes by letting, for example, the collective diffusion coefficient depend on the volume fraction of polymer, i.e., \( D_{\text{coll}} = D_{\text{coll}}(\epsilon) \). Besides its relevance from a fundamental standpoint, the understanding, and subsequent control, of the swelling kinetics is of major importance in two practical situations: actuators (50–52) and drug delivery systems (see, e.g., References 53 and 54 and references therein).

4. INSTABILITIES IN GELS

4.1. First Observations

As mentioned previously, the swelling process is, in many cases, inhomogeneous in space. Because cross-linked polymeric networks have elastic properties, strains and stresses develop within the gel in response to the spatial change in the volume variation. Because gels can undergo huge volume variation, those stresses can become large enough to destabilize the swelling sample. Indeed, the existence of patterns in swollen gels has been known since the nineteenth century, in the context of photographic gelatin films (55–57). Tanaka also reported that, during swelling, transient patterns formed at the surface of gels. When a sample of gel is put into a solvent, sharp creases quickly form at the surface of the gel. The characteristic spacing between those creases increases in time until they eventually disappear when the sample has reached its final size (58). Tanaka also recognized that those patterns could be made permanent by geometrically constraining the swelling gel. The bottom side of a gel layer is chemically bound to a rigid substrate and left for swelling. Because of this confinement, compressive stresses build up and the creases initiated when the free surface is brought in contact with the solvent do not disappear but instead reach a final size (59). These discoveries highlighted the necessity to take into account the nonlinear character of the polymer network’s elasticity. As mentioned previously, because the link with the poroelastic theory has been recognized only recently, the collective diffusion model was first extended to the nonlinear case. Suo and coworkers recently extended the poroelastic theory of gels within the nonlinear range (40, 41, 60). At the thermodynamic equilibrium, this nonlinear theory happens to be a special case of a more general theory written by Gibbs in 1878 (61).

4.2. Geometrically Confined Layer: The Creasing Instability

Since the pioneering work of Tanaka, the problem of crease formation has received considerable attention. Immediately following this observation, a wealth of theoretical (47, 62, 63), numerical (64–67), and experimental papers (68–70) were published, clearly establishing the elastic origin of this instability. In particular, the side observation of the cusped pattern’s evolution (70) allowed a detailed characterization of those singular structures, and a number of key observations were made. Very fine folds initially form at the gel surface. The shape of the surface can be described as a series of circular arcs, of width \( W \) and height \( H \), forming singular points or cusps at their junctions. Below those junctions, there is a folded region, of depth \( D \), where two segments of the free surface are brought into contact during the swelling process (Figure 2). It was found that the number of folds decreases monotonically in time. Because no lateral motion of the cusps was observed, the (discrete) decrease in fold number was ascribed to the annihilation of existing cusps, rather than a merging of adjacent cusps. Concerning the typical dimensions of the pattern, it was found that the width \( W \), height \( H \), and depth \( D \) had the same time dependence, increasing as the square root of time. This is coherent with a diffusive
process, as expected for the highly hydrated gels used in the experiments. Consequently, the aspect ratio $H/W$ remains constant throughout the evolution of the cusp, thereby establishing that the growth of the cusp pattern is self-similar. Furthermore, the ratio $H/D$ was found to be approximately 1. In three dimensions, it was additionally found that the cusps initially formed a tree-like structure before evolving toward a honeycomb pattern (59, 68, 69, 71) (Figure 3). From a numerical standpoint, simulations of models combining the THB collective diffusion model with nonlinear elasticity have proven themselves sufficient to reproduce both the reported annihilation process and honeycomb-like cusped patterns. From a theoretical standpoint, Onuki (47) performed a detailed analysis of a similar model. He clearly established the existence of a linear instability above a threshold in volume variation. Here again, it turns out that a closely related problem of an elastic half-space in compression had been considered theoretically by Biot in 1963 (72). An experimental observation of a creasing instability had also been reported in swollen rubber at a swelling ratio of 2.5 by Southern & Thomas (73). In the absence of any small-scale effects, Onuki recovered a puzzling result of Biot's analysis: The most unstable mode has zero wavelength. The associated penetration length of the instability being also zero, this type of instability is referred to as a surface or Biot instability. Onuki realized, however, that this result could be regularized by taking density correlation into account, yielding a finite but very small wavelength (compared to the thickness of the swelling layer) that grows extremely fast (compared to the timescale of the experiment). Furthermore, Onuki showed that the linearized equations admit finite amplitude cusp-like solutions by forcing a segment of the free surface to be in self-contact. Despite the elegant simplicity of these results, Onuki himself highlighted two important limitations to his model, that is, the impossibility of calculating both the wavelength of the pattern and the depth of the cusp (or equivalently the length of the free surface in contact with itself). Onuki ascribed those limitations to the linear character of his analysis. Further comparisons with the experimental results were unfortunately hindered by the experimental procedures that, at that time, essentially revealed the strongly nonlinear evolution of a pattern induced by a strongly heterogeneous swelling process. In particular, this contrasts strongly with most theoretical works where a layer is assumed to swell homogeneously until it becomes unstable over some threshold in compressive stress.

Recently, however, highly controlled experiments have been performed by several groups to precisely determine the threshold as well as the structure of the instability at threshold. By using submillimeter acrylamide gel films bound to rigid substrates, Hayward and coworkers (74) have shown that the creasing instability arises when the thickness of the thin layer reaches two...
times its initial value $h$. Furthermore, at threshold, the wavelength of the instability was found to be of the order of the sheet’s initial thickness, in opposition with Onuki’s prediction. In another study (75), it was proven using confocal microscopy that those sharp creases are indeed folds within the gel. This experiment unambiguously proved that the origin of the instability does not lie in the heterogeneity of the swelling process but is solely a consequence of the confinement at the bottom of the layer. However, for thin enough films, the instability can be suppressed due to surface tension effects becoming high enough, according to the authors (76).

Soon after the publication of those experimental results, an explanation to the wavelength selection problem of a growing layer on a soft substrate was provided by Ben Amar & Ciarletta (77). In this paper the authors analytically showed that the Biot instability is regularized by surface tension (or inhomogeneities of the swelling process), leading to a wavelength of the order of the thickness with a weak (logarithmic) dependence on the surface tension and gel stiffness. Because this calculation was performed within the framework of the prescribed volumetric strain theory, intended to describe biological growth, the threshold thickness was found to be slightly above the experimental value. Nonetheless, the formalism developed in this

Confocal microscopy: an optical imaging technique that can produce micrographs with a small depth of field (~400 nm) called optical sections.
article enables an extension to more general strain-energy functions. Indeed, it was soon extended by the same group (78) to the case of a swelling gel (i.e., a growth at a constant chemical potential rather than a fixed volume). In this case, the wavelength $\lambda$ scales as

$$\lambda \sim 4\pi h / \log \left[ \frac{\beta h}{\ell} \right],$$

where $\ell = \sigma / \mu$ is the capillary length of the substrate and $\beta$ is a constant depending on the strain-energy density of the layer ($\beta = 32.246$ for a growing Neo-Hookean material and $\beta = 44.953$ for a swelling gel). The critical swelling ratio was found to lie between 1.5 and 3, depending on the underlying mechanism of volume variation. Other theoretical and numerical analyses found a swelling ratio between 2.5 and 3.4 (79). As stated in those various theoretical studies, the creasing instability is thought to form as the result of strong nonlinear effects arising above the threshold of the linear instability, in agreement with the previous experimental observations (69, 70).

The recent experimental results of Hayward and coworkers (74), however, claim otherwise. Indeed it was found that the pattern does not appear to form through the nonlinear evolution of a sinusoidal undulation that would fold over itself at a finite distance from the threshold of instability. Instead, it appears that “fully-formed creases nucleate and grow across the gel surface” (74, p. 367). This observation has been confirmed by the same group using a different experimental setup (35). In those studies, the three-dimensional patterns formed near the threshold are not hexagonal cells but rather are made of sharp lines with occasional branching points, although three lines are usually seen to merge at those junctions (as in tree-like and honeycomb patterns). The creases have been found to grow laterally until they connect with other lines (Figure 4). By manipulating the density of defects within the gel, the authors have shown that a higher number of defects yields a corresponding shortening of the average crease length. The authors also highlighted the existence of a hysteresis for the threshold of crease formation and disappearance. However, it could not be ascertained whether crease disappearance was a continuous or discontinuous process, as suggested in Reference 80. Another group has investigated experimentally the formation of creases in a polymer layer under the action of an electric field, which creates a compressive stress. Although creases also appear suddenly, the creases evolve to form craters rather than tree-like or honeycomb patterns (81).

Together, those observations strongly hint at a subcritical bifurcation. Slightly different experiments have been conducted by Guvendiren and coworkers on swelling films with depth-wise cross-linking gradients and might shed light on this important distinction from the previous experimental results. Using chemical treatments, they designed thin films with an upper layer, of variable thickness, softer than the bulk (82). Upon swelling, the surface developed a smooth undulation, or wrinkling instability, that entered in self-contact with increasing volume, leading to the formation of folds (83). Furthermore, the reported instability threshold was significantly lower than in Reference 74.

The formation of a soft skin at the free surface of hydrogels is known to occur naturally because oxygen inhibits the gelification process, and this effect might have been more pronounced due to different experimental protocols in past experiments such as those described in Reference 69, where polymerization was performed with the free surface in contact with air. In any case, given the diversity among the experimental results, for both the threshold in compression as well as the exact nature of the transition, we cannot rule out, at the moment, the possibility that the instability may be either subcritical or supercritical depending on the exact composition and relative stiffnesses of both the bulk and the surface of the material.
Recent numerical calculations conducted by Suo and coworkers (84) extended Onuki’s analysis in the nonlinear range and investigated the deformations of a Neo-Hookean half-space in which free surface is forced into self-contact. Here, again, the energy of a cusped structure was found to be smaller than a homogeneous deformation over some threshold in compression, although no prediction could be made on the periodicity or depth of the patterns. The threshold in compression was predicted to increase weakly, as \( h^{1/2} \), with increasing initial thickness \( h \) of the film, in opposition with the results of References 77 and 78. Comparisons with the experimental results (35) yield values of the surface tension of approximately 10 \( \mu \text{N.m}^{-1} \), two orders
of magnitude smaller than other reported values (85). Further theoretical studies would therefore be highly desirable if they ascertained the validity of the model.

As a digression, let us remark that heteroepitaxial film also exhibits cusp formation during growth, a so-called Asaro-Tiller-Grinfeld instability (86, 87). In this case, however, the instability is not purely elastic in origin and arises when a solid film in contact with its vapor (or melt) is subjected to a nonhydrostatic stress, due to mass transport at the free surface. In particular, the Asaro-Tiller-Grinfeld instability arises in both tension and compression. Within the framework of linear elasticity, several authors have established a correspondence between the stress fields of such deformed thin films and those of periodic arrays of cracks (88). In the same spirit, an analogy has recently been drawn (77) between the cusps at the free surface of solids and the free-surface cusps observed at the surface of liquid flows at low Reynolds numbers (89).

4.3. Bent Rods and Tubes: The Kink Instability

Although subcritical bifurcations are not common in elasticity, a similar creasing instability has been observed in 1999 by Gent & Cho in the closely related problem of a bent thick rubber block (90), and many attempts have been made to explain the experimental results (91–96). A bent tube is also known to ovalize and develop a rather singular structure known as a kink; this is known as the Brazier instability (97, 98). Singular kinks in bent gel rods have been found experimentally to form in a catastrophic way (99). Using high-speed visualization, Ghatak & Lal Das (99) have shown that the formation of a finite amplitude kink occurs in approximately 4 ms and is accompanied by the formation of bulges on both sides of the kink. The bulges then propagate at a uniform speed away from the kink. The speed was found to increase with the shear modulus of the gel as \( \sqrt{\mu / \rho} \), \( \rho \) being the density of the gel, similarly to traditional shear waves in elastic media (Figure 5).

Recently, Hohlfeld & Mahadevan have performed analytical and numerical calculations that confirmed this experimental observation (80). They investigated the deformation of a bent Neo-Hookean strip coated with a thin Euler-Bernoulli beam. It was found that, on loading, a finite amplitude kink forms suddenly at a threshold lower than Biot's prediction. Additionally, the kink is found to form with “a rolling, not snapping” motion (80, p. 3). Interestingly, they also found that, on unloading, the depth of the kink should decrease continuously to zero in the limit of vanishing surface energy.

4.4. Flexible Confinement: The Wrinkling Instability

In the previous discussion, the stiffness of the substrate was assumed infinite. However, the case of a swelling film of stiffness \( \mu_f \) bound to a very soft elastic substrate of stiffness \( \mu_s \) has also drawn some attention (100). In contrast with the previous case, the system bifurcates at a very low threshold and develops large wavelength instability (compared to the thickness of the swelling layer). In the vicinity of the threshold, the two interfaces of the oscillating ribbon remain approximately parallel. Later on, the free surface enters in contact with itself, thereby breaking the top-bottom symmetry. Quantitative measurements have been conducted in a two-dimensional geometry and have revealed the following scaling law for the wavelength of the instability \( \lambda \):

\[
\lambda \propto h \left( \frac{\mu_f}{\mu_s} \right)^{1/3}.
\]
Figure 5

(a–j) Kink instability in a bent gel rod of diameter 20 mm. The stiffness of the gel is 15 kPa. Concomitantly with the formation of the kink, two bulges appear and propagate away from the kink. Images are reprinted with permission from Ghatak A, Lal Das A. 2007. Phys. Rev. Lett. 99:076101 (Reference 99). Copyright 2007 by the American Physical Society. (k) A bent slab of PDMS (polydimethylsiloxane) forms a kink at a critical compression. (l) Bifurcation diagram established by Hohlfeld & Mahadevan (80). In the limit of the coating’s vanishing bending energy, the bifurcation diagram has a T shape, with a discontinuous transition on loading and a smooth decrease of the kink’s depth upon unloading. Lowercased letters in black circles, a b, and c, indicate the position of the insets. The color scale refers to the strain-energy density (magnified by the factor indicated in the insets). Unit is the shear modulus of the elastomer. Panels k and l are reprinted with permission from Hohlfeld E, Mahadevan L. 2011. Phys. Rev. Lett. 106:105702 (Reference 80). Copyright 2011 by the American Physical Society.
In fact, this scaling law is not only applicable to gels, and indeed identical behaviors have been reported, for example, for thin metallic films bound to soft elastomer substrates. On cooling or heating the system, the mismatch in thermal dilatation induces the generation of residual stresses that may be strong enough to destabilize the structure. Such a scaling law can actually be found without solving the full equations of equilibrium. By treating the swelling layer as a Föppl-von Kármán plate bound to a linear substrate, one may derive Equation 8 (101). The Föppl-von Kármán model has also been applied to the study of a free-standing thin swelling layer clamped on one side (102). Within the framework of the Föppl-von Kármán approximation (103, 104), it is also possible to investigate the strongly postbuckling regime. The physics behind this problem has been discussed extensively in the literature (105–111) and is not restricted to the case of swelling gels. The value of the proportionality coefficient, however, depends on the system under consideration and is lowered for swelling gels (78, 112). This is due to the decrease in the effective elastic modulus as a consequence of the swelling process that decreases the volume fraction of cross-linkers. In many biological cases, however, such as the formation of fingerprints or tubular organs (113), the stiffness of the substrate is not much smaller than that of the swelling layer, and the situation is intermediate between the scaling laws (Equations 7 and 8). A detailed analysis reveals that the relation (Equation 8) is a good approximation (with a relative error of less than 5%) for swelling layers 10 times stiffer than the substrate. Equation 7 is correct when the stiffness of the substrate is at least twice that of the swelling layer, while in the intermediate range, a more complex relation is involved (78).

Another effect of major importance for the development of instabilities in swelling or growing layers is the initial curvature of the layer, in comparison with its thickness. It was found theoretically to be a stabilizing effect in two dimensions (78), and was recently confirmed experimentally (112) (Figure 6). In three dimensions, when a thin layer of gel swells on a soft substrate, it develops smooth undulations, similarly to the two-dimensional case, although with no preferential directions (100). In a curved geometry, however, because curvature is a stabilizing effect, buckling is initiated in the regions of smallest curvature and the buckles are oriented in the direction of the smallest radius of curvature (113, 114).

4.5. Shrinking Patterns

Although the cusp instability, possibly arranged in an hexagonal array in two dimensions, is the hallmark of gel swelling, either as a transient or permanent structure, constrained shrinking gels exhibit a zoo of morphologies, most of which are transient. Essentially two geometries have been considered: a shrinking rod in which extremities are fixed and a layer in which lower surface is bound to a substrate.

In 1992, Matsuo & Tanaka investigated the shrinking process of thin gel rods (with diameters in the millimeter range) in which extremities are clamped (115). When immersed in an acetone-water solution, the rod shrinks and develops nontrivial patterns depending on the initial stretching or compression of the gel, as well as on the concentration of acetone. Essentially three modes of deformation were reported. In the absence of initial strain, for low acetone concentration, the rod radius shrinks homogeneously until it reaches a threshold and develops a wavy pattern, the bubble pattern, with more or less well-arranged alternating solvent-rich and polymer-rich sections. In this case the wavelength of the pattern is proportional to the radius of the rod. At moderate acetone concentration, cross-sectional opaque planes are seen to appear throughout the rod, forming the so-called bamboo pattern. The thickness of those planes is estimated to be of the order of the light wavelength, and their spacing scales as the square root of the gel radius. At higher acetone concentration, the gel becomes opaque and wrinkled.
When the rod is initially stretched (respectively compressed), higher (respectively lower) acetone concentration is needed to observe the bamboo and tube patterns. Qualitative arguments were developed to understand those patterns.

The general idea is that because only the outer layer of the gel is in contact with the solvent, it shrinks first, eventually becoming impermeable. Once a dense impermeable skin is formed at the surface of the rod, the evolution of the system occurs at a constant volume. According to Matsuo & Tanaka, the system relaxes under this constraint and falls below its spinodal line where two situations arise. If the skin is flexible, the radius of the gel collapses at periodic locations, forming bubbles along the rod. In contrast, if the gel is stiff enough, either collapsed cross-sectional planes or surface instabilities should arise. On the basis of the nonlinear collective diffusion model, those results were later analyzed more quantitatively by

---

**Figure 6**

(a) Buckling of a swelling gel layer bound to a soft compliant substrate. Image reprinted with permission from ASME for paper by Sultan E, Boudaoud A. 2008. *J. Appl. Mech.* 75:051002 (Reference 100). Copyright 2008 by ASME. (b–i) Transition from the buckling to the creasing instability. A ring of swelling gel is bound to a disc of neutral gel. When immersed in water, only the outer ring swells. By increasing the stiffness of the inner disc, the instability becomes progressively condensed at the free boundary. (b–e) Various experiments with similar initial aspect ratios and increasing values of $\mu_f/\mu_s$. (f–i) Corresponding theoretical predictions. Although the absolute amplitude of the deformation is not given by the stability analysis, the relative amplitude (between the inner and outer interfaces) shows a condensation of the deformation at the free boundary. Panels b–i are reprinted with permission from Dervaux J, Couder Y, Guedeau-Boudeville M-A, Ben Amar M. 2011. *Phys. Rev. Lett.* 107:018103 (Reference 112). Copyright 2011 by the American Physical Society.

When the rod is initially stretched (respectively compressed), higher (respectively lower) acetone concentration is needed to observe the bamboo and tube patterns. Qualitative arguments were developed to understand those patterns.

The general idea is that because only the outer layer of the gel is in contact with the solvent, it shrinks first, eventually becoming impermeable. Once a dense impermeable skin is formed at the surface of the rod, the evolution of the system occurs at a constant volume. According to Matsuo & Tanaka, the system relaxes under this constraint and falls below its spinodal line where two situations arise. If the skin is flexible, the radius of the gel collapses at periodic locations, forming bubbles along the rod. In contrast, if the gel is stiff enough, either collapsed cross-sectional planes or surface instabilities should arise. On the basis of the nonlinear collective diffusion model, those results were later analyzed more quantitatively by
Boudaoud & Chaieb (116). In particular, no spinodal decompositions were needed to understand those patterns. Rather, a stability analysis was sufficient to establish a phase diagram of the instabilities, as well as a correct description of the radius dependence of the patterns. According to this analysis, if the polymer network is not ruptured during the deformation, the patterns should be transient and the rod should ultimately resume a cylindrical form. This is consistent with the fact that a rod in tension is stable (this is true for most elastic material), and this is in agreement with the observations of Reference 115. Transient bubble patterns have also been reported during the shrinking of gel beads (68). Similar patterns have been reported in shrinking gel layers whose bottom surfaces are chemically bound to a substrate (117). After polymerization, thin constrained layers are immersed in water, where they are left for swelling until they reach equilibrium. During this process, as mentioned previously, they develop a honeycomb-like pattern of folds. Upon shrinking, the network of folds evolves depending on both the acetone concentration and the initial degree of swelling, forming bubble or grain patterns. Those patterns, however, are transient. When the system reaches equilibrium, the thin layer becomes flat again. On the theoretical and numerical sides, however, such patterns are still poorly understood.

4.6. Prescription of Metrics on Surfaces

Besides confined environment, other processes such as the heterogeneity of the swelling process can induce the formation of nontrivial patterns in gels. Indeed, spatial variations in the degree of swelling require the development of stresses and strains to accommodate the incompatible local volume variations. We mentioned previously some examples of patterns induced by inhomogeneous swelling fields, although such patterns were transient. However, because the degree of swelling can be chemically modulated, it is possible to design a gel that, at equilibrium, has swollen heterogeneously. When the degree of swelling of the gel changes in space, the volume variation is incompatible and the system must deform to accommodate this swelling program. Such experiments require fine control over the polymerization protocol and have been performed only recently.

Because one of their dimensions is small compared to the others, thin structures may be approximated by surfaces and, in this geometrical limit, it was postulated that the prescription of a swelling field may reduce to the prescription of distances between points on a surface, that is, a prescribed metric. However, because an unconstrained swelling process is in general isotropic, it can be described by a scalar field, and instead of using a tensorial quantity (the metric), the information contained within the metric tensor is better expressed in terms of the Gaussian curvature. Exploiting this idea, Sharon and coworkers investigated the effects of prescribing a positive or negative Gaussian curvature to a thin disc, using thermosensible acrylamide gels (118). A disc of gel with a radial distribution of monomers is first polymerized. Upon heating of the system, the gel undergoes a swelling transition at a critical temperature and deforms spontaneously. When a positive curvature is prescribed, dome-like structures are observed, which indeed possess a positive curvature close to the prescribed value everywhere on the surface. However, when a negative Gaussian curvature is prescribed, the disc adopts wavy configurations with important variations (larger than the mean value) of the Gaussian curvature. The reason for this important distinction between those two cases can be understood if one takes into account the bending energy within the energy balance. Because surfaces of negative Gaussian curvatures do not preserve the axial symmetry, they generate surfaces with important mean curvature that contribute significantly to the overall elastic energy. To minimize its elastic energy, the disc deviates from the prescribed Gaussian curvature by developing
small-scale structures, therefore decreasing its bending energy, at the cost of some increase in its stretching energy.

Following these observations, several papers have been published on the deformations of thin samples subjected to arbitrary growth fields (119–122). Because of their generality, such models allow one to investigate closely related problems of biological growth of thin samples such as leaves, petals (M. Ben Amar et al., submitted manuscript), or algae (119, 123, 124), where shape selection results from the minimization of an elastic energy. In particular, the anisotropy of the growth field has been found to be of crucial importance for the formation of patterns in algae. Furthermore, when the principal direction of the growth field does not coincide with the plane of the thin sample, it can induce a preferential mean curvature, in addition to the preferential Gaussian curvature. The previous physical theories, however, used the framework of volumetric growth rather than one of swelling. Although it is established that there are substantial discrepancies between the two models in the limit of large deformations (78), it is yet unknown whether this affects substantially the patterns within the geometrical limit of very thin samples (Figure 7).

5. DISCUSSION AND PERSPECTIVES

Thanks to their swelling property, gels allow one to investigate the process of volumetric growth in the limit of large deformations. Their nonlinear behavior is responsible for the formation of complex patterns that are not fully understood. Besides their ever-increasing number of practical applications, gels provide a promising path toward the understanding of biological growth. This proceeds from the fact that many biological objects have a gel-like structure.

Indeed, although living matter is essentially made of water, it does not behave as a fluid at the tissue scale on a wide range of timescales. A first (natural) explanation to this counterintuitive observation is provided by the existence of cells. Crudely speaking, water is packed within impermeable elastic bags, the plasma membranes, which are bound to each other by strong adhesive junctions. Although such a network still viscously dissipates some energy when deformed, it does not flow anymore (if the applied stress does not overcome the strength of adhesive junctions) and can recover its initial configuration when loads are removed. This picture, oversimplified for the purpose of illustration, is partly correct for some biological tissues such as epithelia. It does put some strong constraints, however, on the cellular motility and hence tissue functions. Complementary to this fascinating architecture, nature can exploit another way of turning water into a solid: gelification. Gels are present in many forms of life as they are the structure of the extracellular matrix in which cells are embedded. Connective tissues, for example, are essentially a highly hydrated network of biopolymers (polysaccharides and proteins). In this case, it provides the scaffold necessary for cellular locomotion, a reservoir of water needed for chemical reactions to occur, and a buffer against external stresses. It also retains nutriments, metabolites, and growth factors. Furthermore, the extracellular matrix dynamically regulates various cellular functions and is involved in several pathologies from fibrosis to cancer invasion. Besides connective tissues, gels make up the vitreous humor of the eye, and cartilage, as well as several biological membranes such as the cornea and basement membranes. In plants, the extracellular matrix is also known as the cell wall and is a cellulose-based gel. The cell walls of bacteria, algae, and fungi are also gel-like structures. Unicellular organisms such as bacteria or yeast that can form colonies also secrete an extracellular matrix, whose functions closely resemble those of multicellular organisms.
Although biological growth is undoubtedly more complex than gel swelling, a clear understanding of the latter should provide some essential tools to apprehend the former. For example, recent experiments have shown that swelling gels develop instabilities that closely resemble the contour instabilities observed during avascular solid tumor growth (112).

In the meantime, several points pertaining to gel swelling remain poorly understood:

- Although much progress has been made to understand the formation of the creasing instability, and in particular the nature of the transition, we are still lacking an integrated theoretical

---

**Figure 7**

(a,b) Swelling of an initially flat disc with a programmed heterogeneous swelling field. (a) The degree of swelling increases with the concentration of monomers, which is a function of the distance from the center. (b) Measured and prescribed perimeter of a circle (respectively solid and dashed lines) on the deformed surface, as a function of the distance from the center. On average, the agreement is correct for both positive (red) and negative (blue) Gaussian curvature discs. Because the surface has a nonzero Gaussian curvature, this relation deviates from a straight line. Panels a and b are taken from Klein Y, Efrati E, Sharon E. 2007. Science 315:1116–20 (Reference 118) and reprinted with permission from AAAS. (c,d) Examples of flowers with nonvanishing Gaussian curvature. (c) A surfinia (Paris). (d) An angel's trumpet [Brugmansia (Morocco)]. Panels c and d are taken from a submitted manuscript by M. Trejo, M. Ben Amar, and M.M. Müller. (e,f) Anisotropic growth of a thin disc. (e) Depending on the ratio of circumferential to radial growth rates, different shapes may be obtained (119). (f) Evolution of the reproductive whorl of a green unicellular alga, Acetabularia acetabulum. During the early stages of its evolution, the growth of the cap is mostly radial. After a short window of isotropic growth, circumferential growth dominates (123). Note the good agreement with the theoretical prediction in panel e. Images in panel f are reprinted with permission from Berger S. 2006. Photo-Atlas of Living Dasycladales. Brest: Carnets de Geologie (Reference 124).
picture describing the profile and depth of a single crease. Furthermore, more experimental studies are needed to investigate the coarsening dynamics of the creases and to quantify the mechanisms of interaction between creases.

- Recent experiments and theoretical work have essentially focused on the static properties of gels. Complex transport mechanisms involving convection might lead to the formation of other types of instabilities, such as channels (125).
- Although the anisotropy of the volume variation process is known to be of paramount importance during biological growth, this effect is still poorly investigated in the context of gel swelling. Nematic gels as well as interpenetrating gel networks might provide a nice experimental tool to study this effect.

**DISCLOSURE STATEMENT**

The authors are not aware of any affiliations, memberships, funding, or financial holdings that might be perceived as affecting the objectivity of this review.

**LITERATURE CITED**

New York: Academic
Contents

Sixty Years of Condensed Matter Physics: An Everlasting Adventure
Philippe Nozières .......................................................... 1

What Can Gauge-Gravity Duality Teach Us About Condensed Matter Physics?
Subir Sachdev ................................................................. 9

Spin Ice, Fractionalization, and Topological Order
C. Castelnovo, R. Moessner, and S.L. Sondhi ......................... 35

Pairing Mechanism in Fe-Based Superconductors
Andrey Chubukov ........................................................... 57

Magnetoelectric Hexaferrites
Tsuyoshi Kimura ............................................................ 93

Studying Two-Dimensional Systems with the Density Matrix Renormalization Group
E.M. Stoudenmire and Steven R. White ................................. 111

Angle-Resolved Photoemission Studies of Quantum Materials
Donghui Lu, Inna M. Vishik, Ming Yi, Yulin Chen,
Rob G. Moore, and Zhi-Xun Shen ....................................... 129

Superconducting Microresonators: Physics and Applications
Jonas Zmuidzinas ............................................................ 169

Phase Change Materials: Challenges on the Path to a Universal Storage Device
T. Siegrist, P. Merkelbach, and M. Wuttig ............................... 215

Quantum Computation by Local Measurement
Robert Raussendorf and Tzu-Chieh Wei ............................... 239

Bose Gases with Nonzero Spin
Masahito Ueda ............................................................... 263
Planetary Atmospheres as Nonequilibrium Condensed Matter
   J.B. Marston .............................................. 285

Mechanical Instabilities of Gels
   Julien Dervaux and Martine Ben Amar ......................... 311

Quantum Coherence in Photosynthetic Light Harvesting
   Akihito Ishizaki and Graham R. Fleming ....................... 333

Physics of Cancer: The Impact of Heterogeneity
   Qiucen Zhang and Robert H. Austin ........................... 363

Errata
An online log of corrections to Annual Review of Condensed Matter Physics
articles may be found at http://conmatphys.annualreviews.org/errata.shtml