Shrinking-induced Instability in Gels

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Polymer gels can undergo a volume phase transition (either continuous or discontinuous) when an external condition such as temperature or solvent composition is altered [1, 2]. This phase transition is either a shrinking or a swelling. We investigate the instability of a tubular fluid gel after shrinking. When gels are immersed in a solvent, the polymer network undergoes a diffusion inducing an osmosis pressure through the gel. A bubble and a bamboo pattern were observed under such conditions (E. sato-Matsuo and T. Tanaka, Nature 358 482 (1992)). In this paper we investigate this pattern formations as a mechanical instability.

The study of the structure and dynamics of self-assembly is a field of growing interest. In particular, shape fluctuations and instabilities of gels and membranes, under equilibrium, or metastability conditions have been the subject of several studies. Pattern forming in swelling and shrinking gels are one of the most amazing patterns one can encounter in complex systems [3, 4]. The polymer gels studied by Tanakas group were cross-linked polymer network immersed in liquid. Various shrinking patterns were classified in form of a phase diagram, and the shape variety was explained in term of macroscopic phase separation. The wavelength associated to two patterns were measured. In Sato-Matsuo and Tanaka [4], cylindrical gels of acrylamide, of various diameters were prepared. Each end of the dried gel was glued to a glass rod; the separation of the tip was varied to control the final length of the cylinder. The gel was allowed to swell in water and, after it reached equilibrium, placed in

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[2]During the submission of this paper, Friend and mentor, Prof. Tanaka passed away. This work would not see the light without his input

an acetone-water. The dependence of the pattern on the acetone composition and final length was investigated. Mainly bubble and bamboo patterns were observed. The bubble pattern resemble the Rayleigh instability known in hydrodynamics. The cylinder is composed of swollen regions believed to suffer tension and shrunken regions suffering compression. At different experimental conditions bamboo patterns appear; they are made of cross-sectional planes consisting the collapsed gel membrane. The wavelength of the bubble was found to scale with the initial radius of the cylinder and the bamboo patterns was found to vary like $\sqrt{R}$.

In this paper, we explain the origin of this dependence of the wavelength of the bamboo and the bubble pattern found in [3] versus the radius of the cylinder in terms of a linear stability analysis. First we will study the bamboo instability, where thin disks appear along the shrunken cylinder. It is to be kept in mind that in this case the skin of the cylinder is rigid and the diameter of the cylinder is constant in time.

Let's consider a cylindrical gel of diameter $2R$ that undergoes the bamboo instability. In figure 1, we display a sketch of such a pattern, where we draw 2λ pattern.

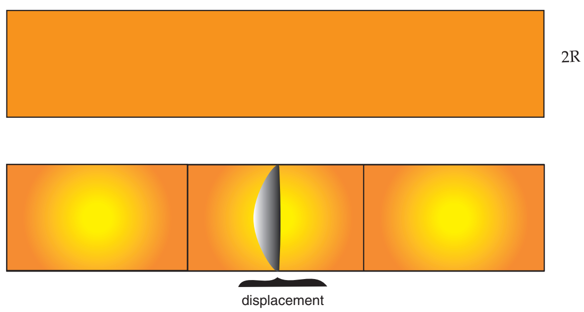

FIG. 1. A sketch of the bamboo instability. The cylinder has a diameter of $2R$. We also displayed the displacement vector u of the gel network.

The generalized deformational free energy of a gel can be written as [5, 6]:

$$\beta G = \beta(G_{\text{spinodal}} + G_{\text{rubber}} + G_{\text{ornstein-Zernick}}) \tag{1}$$

where, using displacement vector $\mathbf{u}$ as in [5],

$$\beta G_{\text{spinodal}} = \frac{\tau}{2} \int d\vec{r} \sum_m \left(\frac{\partial u_m}{\partial x_m} \right)^2 \tag{2}$$

$$\beta G_{\text{rubber}} = \frac{\mu}{2} \int d\vec{r} \sum_m \left(\alpha_z^2 \left(\frac{\partial u_m}{\partial z} \right)^2 + \alpha_r^2 \left(\frac{\partial u_m}{\partial x} \right)^2 + \alpha_r^2 \left(\frac{\partial u_m}{\partial y} \right)^2 \right) \tag{3}$$

and

$$\beta G_{\text{ornstein-Zernick}} = \frac{\kappa}{2} \int d\vec{r} \left[\vec{\nabla}.(\vec{\nabla}.\vec{u}) \right]^2 \tag{4}$$

In equation 3, α_z, α_r are the elongation ratios in the longitudinal and transversal directions respectively. In equation 4 κ can be seen as the stiffness of the gel. Since the pattern observed in cylindrical gels is periodical, we will expand the displacement $\vec{u}$ in Fourier component, keeping in mind that $\vec{u} = (0, 0, u_z(z, r))$. We have:

$$u_z(z, r) = \sum_{k,q} u_0(k) \exp(iqr + ikz)$$

Where $q = \frac{(n+1/2)\pi}{R}$ and R is the radius of the cylindrical gel. Equation 1 will write:

$$\beta G = \frac{V}{2} \sum_{k,q} \left(\mu\alpha_r^2 q^2 + (\tau + \mu\alpha_r^2 + \kappa q^2)k^2 + \kappa k^4 \right) u_0^2(k) = \sum_{k,q} \alpha(k,q) u_0^2(k)$$

The linear instability appears for $\alpha(k,q) < 0$. The condition $\alpha(k,q) = 0$ gives the threshold of the instability and the value of τ at the onset of the instability, one gets:

$$q_c = q_0 = \frac{\pi}{2R}$$

$$k_c = \left(\frac{\mu\alpha_r^2}{\kappa} \right)^{1/4} q_0^{1/2} \tag{5}$$

and

$$\tau_c = -(\mu\alpha_z^2 + \kappa q_0^{1/2})$$

In Figure 5 of reference [4], the bamboo pattern has wavelength so that $\lambda \sim 0.032\sqrt{R}$. From this fit we find that $\frac{2\sqrt{\pi}}{(\mu\alpha_r^2/\kappa)^{1/4}} = 0.032$

In the following, we will describe the bubble instability taking into account the flexibility of the outer skin of the cylinders in [3]. A scheme of the instability is in figure 2.

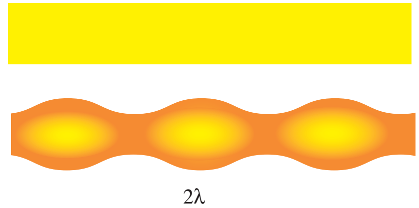

FIG. 2. A schematic view of the bubble instability. The wavelength is the distance between the antinode. Here we displayed 2λ

The deformation energy can be written:

$$\begin{aligned}
\Delta G &= \frac{k_B T}{2}\int_{\mathrm{total}}\left[\tau(\phi-\phi_0)^2+\left({\alpha_z}^2\left(\frac{\partial u}{\partial z}\right)^2+{\alpha_r}^2\left(\frac{\partial u}{\partial r}\right)^2\right)+K\left(\nabla\phi\right)^2\right]dr \\
&+ \frac{k_B T}{2}E(\Delta R)^3\int_{\mathrm{skin}}(\Delta u)^2 dr
\end{aligned}$$

u is the displacement vector and ϕ the polymer density.

The first term is the Flory-Higgins term, the second is the shear deformations term (induces long wave lengths) and the third term is the Ornstein-Zernick term (large wave lengths) the last term is the skin term which favors long wave length.

The term involving ϕ is responsible for the spinodal decomposition.

$\phi = \phi_0(1-\nabla\cdot u)$ with local free energy:

$f(\phi) = f(\phi_0)+\tau/2(\phi-\phi_0)^2+\cdots\ \tau<0 \to$ spinodal decomposition

Suppose $u = (\frac{x}{r}u_r, \frac{y}{r}u_r, u_z)$,

where $u_r = u_r^0\cos(kz)\sin(qr)$ and $u_z = u_z^0\sin(kz)$ then

$$\begin{aligned}
\Delta G &= V_b\tau_b\left((kR)^2 u_z^{0\,2}+4\left(\frac{\Delta R}{R}\right)(kR)u_z^0 u_r^0 + C u_r^{0\,2}\right) && (6)\\
&+ \frac{V_s}{2}\left(\left((\tau+\nu_s{\alpha_z}^2)(kR)^2+E\left(\frac{\Delta R}{R}\right)^2(kR)^4\right)u_z^{0\,2}\right. && (7)\\
&+ \left.(\nu_s{\alpha_z}^2(kR)^2+E\left(\frac{\Delta R}{R}\right)^2((kR)^4+1))u_r^{0\,2}\right) && (8)\\
&= A u_z^{0\,2}+2Bu_z^0u_r^0+Cu_r^{0\,2} && (9)
\end{aligned}$$

Clearly the instability occur if $B^2-AC>0$

We find that $k\sim\frac{1}{R}$ or $\lambda\sim R$

We can also, study the instability as a hydrodynamic instability of the skin of the gel. Here we suppose that the cylinder is hollow and that the skin that has a bending modulus is responsible for the instability when it is in competition with the osmotic pressure forcing. In this following model, we consider that the only length scale in the problem is R, which is not entirely true, as we will see in a future work [10]. We will focus on the cylinders whose length has increased or remained unchanged (Fig. 3 in [3]). The mechanical instability is induced by an osmosis pressure due to the diffusion of the polymer network into the solvent [4, 7, 8]. In the following we will show that when the gel shrinks, while keeping its volume constant, the competition between the compression stress and the curvature of the cylinder are responsible of the wavelength selection. First of all, we point out that the cylinders suffering the bubble instability are hollow, and can be seen as a hollow shell whose mean curvature is H and its curvature energy is :

$$E_b = \kappa \int ds H^2 \tag{10}$$

where κ is the bending stiffness of the cylinder membrane. In equilibrium, the cylinder has no tension, but during the shrinking instability, the membrane will suffer a tension, especially in the region of the cylinder which look like ellipsoids and where the gel looks stretched (See Fig. 1 of [3]). The " surface energy" looks like:

$$E_s = G \int ds \tag{11}$$

where G is similar to a surface tension and is analog to surface tension in the case of fluid membranes and liquids [9].

We will assume small axisymmetric deformations of the gel from its cylindrical shape conserving the total volume. The local circular circular radius $R(z)$ is written as

$$R(z) = R + u(z) \tag{12}$$

Let's write the radius as a function of its fourier transform, since we assumed axisymmetric deformations

$$u(z)=\sum_q u_q e^{iqz} \tag{13}$$

The conservation of volume will allow us to express the radius R as a function of its original radius R_0, we have

$$R(z)=R_0(\sqrt{1-|u_q|^2}+(\frac{u_q}{\sqrt{2}}e^iqz+c.c) \tag{14}$$

In cylindrical coordinate the mean curvature becomes:

$$H=\frac{1}{R\sqrt{1+R'^2}}-\frac{R''}{(1+R'^2)^{3/2}} \tag{15}$$

where $R'=dR/dz$ and the surface element becomes $ds=2\pi R\sqrt{1+R'^2}dz$ The total free energy looks like for small deformations that is $R'<<1$

$$E=E_b+E_s \tag{16}$$

Where

$$E_b=\pi\kappa L/R_0+\frac{\pi\kappa L}{R_0^3}\sum_q(\frac{3}{2}-\frac{1}{2}(qR_0)^2+(qR_0)^4)|u_q|^2 \tag{17}$$

and the energy associate to the tension writes

$$E_s=E_{s0}+\pi GL/R_0\sum_q(1-(qR_0)^2)|u_q|^2 \tag{18}$$

The threshold of the instability occurs when the term proportional to $|u_q|^2$ is zero an that gives

$$q_cR_0\sim 1 \tag{19}$$

for $G\ll 2\kappa/R_0$

This is in agreement with the results of [3], where it was found that $\lambda\sim 1.4R$ A more sophisticated model will be the subject of a future publication [10]

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