Diffusion-mechanical instability of a spherical gel

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Résumé. Lorsqu'une sphère composée de polymères hydrophiles est immergée dans de l'eau, celle-ci gonfle. Dans le cas de sphères en polyacrylamide, le rapport entre le volume final et le volume initial peut augmenter d'un facteur de l'ordre de mille et ce processus de gonflement est non linéaire. Nous présentons une étude expérimentale du gonflement de ces billes dans de l'eau. Au cours de la croissance, une instabilité liée à la diffusion de l'eau et à la déformation élastique de la sphère est observée et analysée. Les motifs à la surface de la sphère sont d'abord aléatoires et homogènes. Ensuite, des rides apparaissent et leurs longueurs d'onde et amplitudes augmentent en fonction du temps. Ces rides prennent d'abord la forme de lobes hémisphèriques puis ceux-ci se déforment. Au fur et à mesure que le temps passe, le nombre de lobes diminue. Enfin, la sphère finale est lisse. Ces résultats sont comparés à des modèles mathématiques de type réaction-diffusion et noyau-coquille.

Abstract. When a sphere made of hydrophilic polymer is immersed in water, it experiences a volume phase transition and swells. In the case of polyacrylamide gels, the volume ratio can increase by a factor of the order of one thousand and this swelling process is nonlinear. We present an experimental study of the swelling of polyacrylamide spheres. During the growth, a diffusion-mechanical instability is observed and analyzed. The patterns on the surface of a sphere are first random and homogeneous. Then, wrinkles appear and their wavelength and amplitude increase as a function of time. The wrinkles were first well defined hemispherical lobes and then deformed. As time proceeds, the number of lobes decreases. Eventually, the sphere is smooth and well rounded. These patterns are discussed in relation to predictions of reaction-diffusion models and in core-shell models.

1 Introduction

Gels are very surprising materials : they are mostly made of liquid, but resist to flow. Examples are from the food we eat to the cosmetic we spread on our skin. Yet there is a large variety of gels and many surprising phenomena are observed everyday and remain unexplained.

When a sphere of hydrophilic polymer is immersed in water, it experiences a volume phase transition. The water diffuses into the sphere and the polymer reacts. Such reaction-diffusion phenomena can lead to pattern formation. Turing and others [1] proposed that the different patterns found when solving the reaction-diffusion system on the surface of a sphere could explain the symmetry breaking which leads to the shape of the embryo or the evolution of tumors. Hence morphological instabilities of such soft swelling spheres may have important implications in order to understand the effect of the domain growth and curvature on pattern selection.

Most of the previous works on pattern transformation in swelling gels by elastic instability concentrated on films [2] and several models were developed. As gel grows by absorbing water, its elastic modulus decreases. Elastic models provide the wavelength of the patterns. Recently, core-shell soft sphere models [3] which describes wrinkle to fold transition into labyrinth folded patterns has been analyzed. Here our contribution consists in the study of the swelling of a single spherical gel. The details of the swelling shows a mechanical instability and the associated kinetics is measured and analyzed.

2 Growth experiments

The dried polymer spheres were obtained from Educational Innovations and the initial diameter of the beads used here is 3.2 ± 0.5 mm. A time sequence of the swelling is presented in figure 1. The experiments

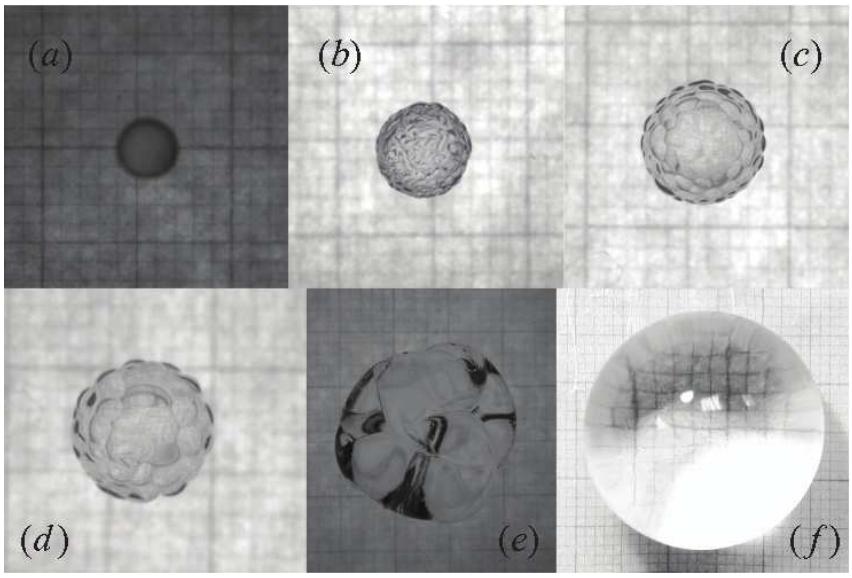

Figure 1. A sequence of images showing the swelling of a polymer particle : (a) the initial dry sphere, (b, c, d, and e) the various patterns observed 2, 5, 10 and 60 minutes, respectively, after immersion, (f) the grown-up hydrogel sphere

are as follows. Initially at $t = 0$, the dry polymer sphere is immersed in demineralized water ; then at given times the polymer sphere is taken out using a spoon, weighed, pictured and immersed again. All the experiments were conducted at room temperature ($T = 22 \pm 0.1°\mathrm{C}$). Using calibrated paper and an imaging software, a measure of the diameter could be obtained. The volume of the sphere increases by a factor of the order of one thousand.

At the beginning the sphere surface is fine having a texture similar to frosted glass (see figure 1(a)). At first wrinkle patterns are observed (see figure 1(b)). Then hexagonal or circular lobes appear and seem to merge (see figure 1(c, d, and e)). The swelling process is not homogeneous. Indeed, the lines between the lobes are due to local shrinking of the gel. The layer at the interfase is under a mechanical constraint, namely, the outer surface of the layer is free to expand, whereas the inner surface is fixed to the core of the sphere. Thus the layer is under opposing demands on the upper surfaces, one to expand and the other to remain partially rigid. Initially, these opposing forces are resolved by stretching the gel unidirectionally perpendicular to the surface. When the osmotic pressure is large the outer surface is forced to buckle. The characteristic wavelength of the pattern must be proportional to the thickness of the swollen layer, as that is the only relevant length scale. As time goes on, the thickness of the swollen layer increases, as does the wavelength of the pattern.

The overall swelling duration until reaching equilibrium takes several hours. During this period, the mass and volume of the sphere increases roughly linearly. The swelling is a multistage process. First, a modification of the polymer surface corresponding to penetration of water molecules into the polymer takes place. The wetting of the shell of the polymer sphere is related to a slight expansion. During this stage, it is supposed that the core remains rigid [4]. Second, the roughness on the sphere surface appears as regularly spaced hexagonal lobes. Third, the number of the wrinkles decrease. Finally, the sphere becomes smooth and well rounded and continue to growth for several hours until reaching the final diameter.

A typical time evolution of the mean diameter is presented in figure 2 where the error bars represent the dispersion from three experiments. Again, three stages can be distinguished during the swelling process. First the dry layer of the polymer in contact with water becomes wet. As soon as the polymer is completely wet, water diffuses into the hydrogel. This is in agreement with the results presented in the inset of figure 2 were the diameter evolves as $t^{0.5}$. At later times, the swelling is well described by an exponential fit. This suggests that the material is relaxing due to visoelasticity (Voigt model).

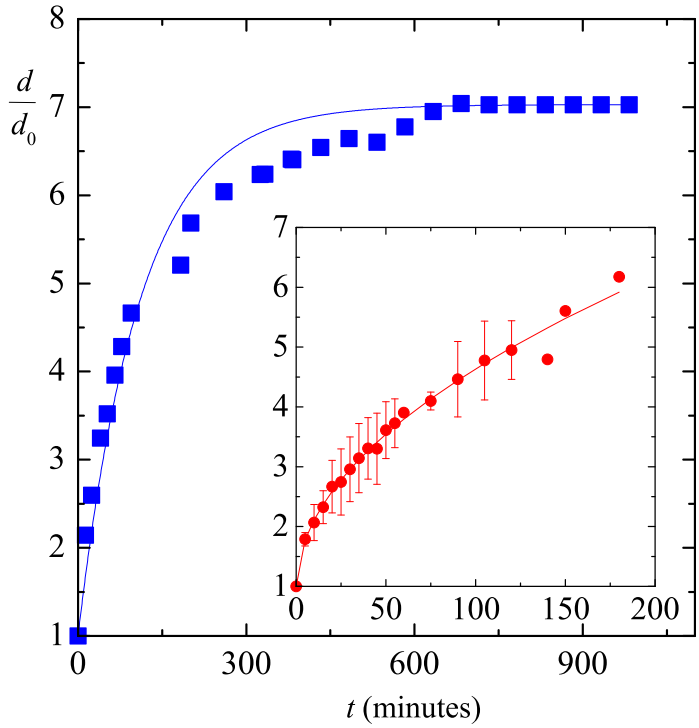

Figure 2. The diameter of the growing spheres as a function of time, the blue line represents an exponential fit. Inset : evolution during the lobed sphere régime, the red line represent a power law fit : $d/d_0 \propto t^{0.5}$

3 Surface pattern analysis

The patterns observed at the growing sphere surface are due to the elastic properties of the material. Indeed, when a wrinkled sphere is cut with a sharp-edged tool, the wrinkle bounce back and disappears.

During the growth of the sphere, two patterns can be distinguished : (i) a wrinkled or lobed pattern (see figure 1(a)) and (ii) and a labyrinth pattern (see figure 1(e)) where the lobes merged is a complicated way. The patterns can be described using the number of lobes or wrinkles and its amplitude (see figure 3). The number of lobes decreases rapidly during the first hour of growth. Then a small number of lobes remains for quite some time before it disappears. Simultaneously, the amplitude of the lobes increases in the first hour and then remain constant for some time. These patterns are observe together with and continuous increase of the diameter of the sphere and change in the properties of the material.

It is suggested that the different patterns (wrinkle and labyrinth) correspond to changes in properties of the sphere, e.g. the ratio of modulus ratio between the shell and the core of the sphere [3]. With increasing deformation, transition to wrinkles to labyrinth patterns were observe. Yet here there is no well defined shell thickness, that is to say that the shell and the core are not two distinct materials.

4 Conclusion

We have presented an experimental study of the swelling of a hydrophilic polymer sphere in water. Specifically, several patterns corresponding to different stages during the growth of the spherical gel were observed. First the pattern contains many wrinkles and folds. Then as water is absorbed the number of lobes decreases rapidly. It seems that some lobes merge and give rise to a labyrinth pattern. The labyrinth pattern relaxes with a longer time scale.

Such hydrogel spheres have been used to study the so called ‘jammed’ state transition of matter or fracture in gels [5], taking advantage of their deformability, friction and optical properties.

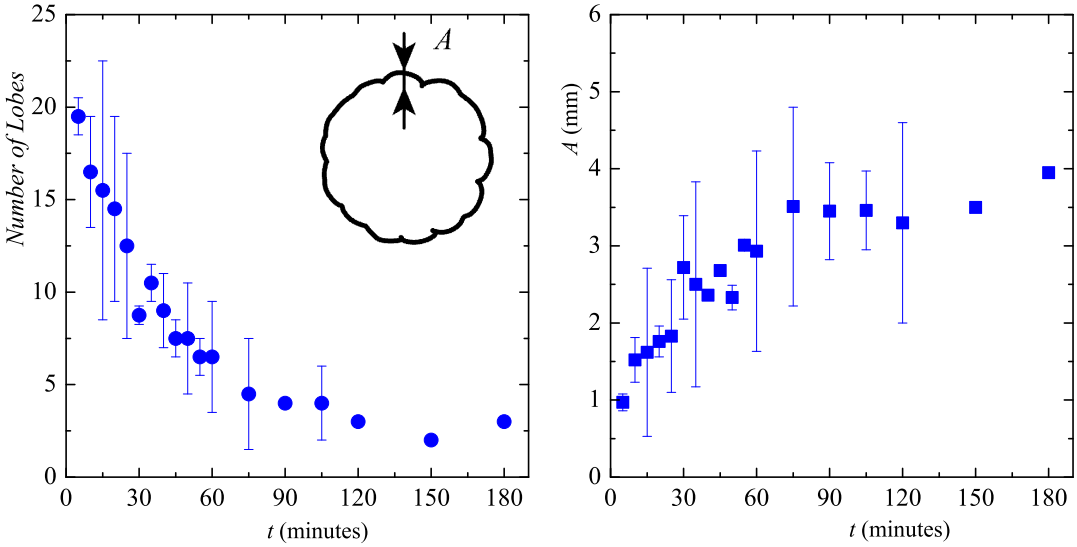

Figure 3. (*left*) Number of lobes and (*right*) amplitude, A, of the lobes around the circumference

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