# Chapter 5

# A Model for Self-Oscillating Miniaturized Gels

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In many works on chemical patterns gels inactive regarding the chemistry involved have been used as reaction medium to suppress hydrodynamic convection while allowing the control of the system far from equilibrium. Instead, in this study, we consider the case of an active gel the behavior of which is influenced by some products of the reaction. We propose a simple model where the gel exhibits mechanical oscillations in response to a chemical reaction.

### Introduction

Gels are cross-linked networks of polymers immersed in a fluid medium. It is now well known that they can exhibit large volume changes in response to many different stimuli: temperature, solvent composition, pH, electric fields. The universality of this volume phase transition of gels has now been clearly established. These stimuli-responsive gels have opened a new field of research by generating numerous experimental and theoretical works; they also pave the way for a variety of new technologies (1).

Since they are open systems that can exchange chemical species with their surrounding solvent, gels can also play the role of chemical reactors. In this framework, the design of open spatial gel reactors has allowed well controlled experimental studies of chemical patterns such as chemical waves or Turing structures (2). They are made of a thin film of gel in contact with one or two continuous stirred tank reactors that sustain controlled nonequilibrium conditions.

In these experiments, the volume of the confined gel is constant; its main role is to damp hydrodynamical motions that would otherwise perturb the chemical intrinsic patterns. More recently it has been shown experimentally that the coupling of a volume phase transition with a chemical oscillator can generate a self-oscillating gel (3, 4). More precisely, if one of the chemical species taking part in the chemical reaction modifies the threshold for the phase transition, then the time periodic variation of this concentration can generate autonomous swelling-deswelling cycles of the gel even in absence of any external stimuli (5, 6). This device thus provides a novel biomimetic material with potential biomedical and technical applications.

The main purpose of this paper is to present a simple theoretical model to describe this interesting phenomenon which provides a further example of the synergy between an equilibrium phase transition and a pattern forming instability. It is based on a Landau type equation for the polymer volume fraction coupled to a simple two variables reactive system that, on its own, can undergo a Hopf bifurcation giving rise to chemical oscillations of the limit cycle type. These oscillating systems have now been extensively studied both from the theoretical and experimental points of view (7).

For the sake of simplicity, we here study gels the dimensions of which are smaller than the characteristic wavelength of the chemo-elastic waves that can also appear in large systems. This enables us to consider homogeneous and uniform systems in agreement with the experiments performed recently on miniaturized oscillating gels.

We have first verified that, in absence of chemical reactions, our dynamical equation for the gel reproduces the dramatic slowing downs in the transition rates which have been observed near the critical point or the spinodal limits of hydrogels. In the last section, we discuss an example of the instabilities that give rise to the self-oscillating behavior of the coupled gel-chemical system and we exhibit corresponding bifurcation diagrams.

### Volume phase transition of gels

We first outline the thermodynamic theory of stimuli responsive gels (8). The free energy is given as a sum of contributions due to the mixing of the solvent and polymer matrix, its elasticity and the presence of counter ions

$$\Delta F = \Delta F_{mix} + \Delta F_{el} + \Delta F_{ion} \tag{1}$$

In terms of the polymer volume fraction  $\phi$ , the Flory-Huggins theory (9) gives

$$\Delta F_{mix} = \frac{kT}{v_1} V[(1-\phi)) \ln(1-\phi) + \chi \phi(1-\phi)]$$
(2)

where V and  $v_1$  are respectively the volume of the gel and the molar volume of the solvent. The polymer-solvent Flory interaction parameter  $\chi$  is a function not only of the temperature but it may also depend on the concentrations of some soluted chemical species (10). On the basis of the simple rubber elasticity theory  $\Delta F_{el}$  can be expressed as

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$$\Delta F_{el} = \frac{3kTV_0v_0}{2} \left[ \left(\frac{\phi_0}{\phi}\right)^{2/3} - 1 - \frac{2}{3}B\ln(\frac{\phi_0}{\phi}) \right]$$
(3)

where  $V_0$  and  $\phi_0$  are the volume and polymer volume fraction in a reference state  $(\phi/\phi_0 = V_0/V \phi/\phi_0 = V_0/V)$  and  $v_0$  the cross link number density. *B* is a debated coefficient which we set to unity according to Flory's treatment.

Finally,  $\Delta F_{ion}$  includes the translational entropy of the counter ions of density  $v_i$ 

$$\Delta F_{ion} = -kTV_0 v_i \ln(\frac{\phi_0}{\phi}) \tag{4}$$

The osmotic pressure

$$\Pi = -\left(\frac{\partial F}{\partial V}\right)_r = \frac{\phi}{V} \left(\frac{\partial F}{\partial \phi}\right)_r \tag{5}$$

plays an important role in volume phase transitions. In the model, it is given by the following explicit expression

$$\Pi = -\frac{kT}{v_1} \left[ \phi + \ln(1-\phi) + \chi \phi^2 \right] + kTv_i \left(\frac{\phi}{\phi_0}\right) + kTv_0 \left[ \frac{1}{2} \left(\frac{\phi}{\phi_0}\right) - \left(\frac{\phi}{\phi_0}\right)^{1/3} \right]$$
(6)

For small values of  $\phi$ , the elastic contribution serves to limit the degree of swelling. The osmotic pressure must be zero for the gel at equilibrium with the surrounding solvent. As shown in Figure 1, by varying  $\chi$ , the gel can undergo a phase transition from swollen to collapsed state (and vice-versa). In such process the system exhibits an asymmetric hysteresis loop. In the case of gels, due to the long range behavior of the elastic energy of deformation (proportional to the volume of the system) the mean-field Van der Waals type theory applies and the transition does not take place at the Maxwell point  $\chi = \chi_m$  where the free energy of the swollen branch becomes equal to that of the collapsed state. It rather occurs at (or near) the spinodal line (11, 12). This leads to observable hysteresis effects in the transition. Indeed experiments have reported differences of temperatures of up to 10 degrees between the temperature at which the collapse occurs and that where swelling takes place. Such hysteresis are also obtained when varying the pH (13, 14). Thermodynamic stability implies that the elastic bulk modulus  $K = \phi (\partial \Pi / \partial \phi)_T \ge 0$ . The condition K = 0 determines the spinodal points  $\chi_{sc}$  and  $\chi_{ss}$  shown in Figure 1. They respectively correspond to the marginal stability points of the collapsed and the swollen state. The locus of these points when the temperature or the solvent composition is varied determines the spinodal curve. The maximum of this curve corresponds to a critical point at which the volume phase transition becomes continuous. When the corresponding osmotic pressure is equal to zero, the system exhibits a critical endpoint at which the first three derivatives of the free energy with respect to V must vanish. Tanaka found such a critical endpoint in a polyacrylamide gel (15). He succeeded in reducing the volume discontinuity at zero osmotic pressure by varying the composition of the solvent.



Figure 1. Equilibrium volume phase transition diagram for the gel. The polymer volume fraction  $\phi$  is represented as a function of Flory's interaction parameter  $\chi$ .

These conditions allow to determine the critical values of  $\phi_c$ ,  $\gamma_c$  and  $\chi_c(T_c)$ . As they are not required in the following we will not give here their values in terms of the parameters defining the free energy. Keeping  $\gamma = \gamma_c$ , near the critical point  $\Pi$  assumes the following standard form  $\Pi = a_0 (\chi_c - \chi) + b_0 (\phi - \phi_c)^3$ , where  $a_0$ and  $b_0$  are constants independent of  $\phi$  and  $\chi$ . One can then define a critical index  $\delta$  such that  $(\phi - \phi_c) \propto |\chi - \chi_c|^{\delta}$  with  $\delta = 1/3$ . Note that here,  $\chi - \chi_c$ , plays a role analogue to that of the magnetic field in spin systems. The bulk modulus tends to zero as  $\chi \to \chi_c$  according to  $K \propto (\phi - \phi_c)^2 \propto |\chi - \chi_c|^{2/3}$ . Similarly near the spinodal points  $\chi_{sc}$  and  $\chi_{ss}$ , the osmotic pressure takes the characteristic expression of a saddle-node bifurcation  $\Pi = a_{si} \Delta \chi + b_{si} (\phi - \phi_{si})^2$  where  $\Delta \chi = |\chi - \chi_{si}|$  with  $i \equiv c$  or s and the bulk modulus now becomes  $K = |\Delta \chi|^{1/2}$ . In general the polymer-solvent interaction depends upon the polymer volume fraction. This is taken into account by a power series expansion  $\chi = \chi_1 + \chi_2 \phi + \chi_3 \phi^2 + \dots$  (16). It has therefore been shown that a strong dependence on  $\phi$  (sufficiently large value of  $\chi_2$ ) can induce a discontinuous transition even in the case of nonionic gels (17).

#### **Relaxation kinetics**

The polymer volume fraction  $\phi$  plays the role of a nonconserved order parameter. In (small) homogeneous and isotropic gels, its time evolution is assumed to satisfy the following Landau type equation

$$\frac{d\phi}{dt} = -\Gamma \frac{\delta \Delta F}{\delta \phi} = -\Gamma \frac{V_0 \phi_0}{\phi^2} \Pi \tag{7}$$

where the kinetic coefficient  $\Gamma$  fixes the time scale. In this description, it is the osmotic pressure that provides the thermodynamic force for the volume phase transition. Obviously, the stationary solutions of Eq. (7) correspond to the thermodynamic states  $\Pi(\phi_s) = 0$ . Within the above model

$$\frac{d\phi}{dt} = \frac{\alpha}{\phi^2} \Big[ (1 - \gamma)\phi + \ln(1 - \phi) + \chi \phi^2 + \beta \phi^{1/3} \Big]$$
(8)

where  $\alpha = kTTV_0\phi_0/v_1$ ,  $\beta = v_0v_1/\phi_0^{1/3}$  and  $\gamma = \left(\frac{v_0}{2} \cdot v_i\right)v_1/\phi_0$ .

For numerical computations we use typical values found in the literature for gels considered in the study of volume phase transitions.

The theory based on Eq. (8) differs from the standard kinetic description of gels volume phase transition which is based on a diffusion-type equation for the displacement vector u(r,t) of a gel element (18). There that linear equation is derived from the theory of elasticity of the gel. It can only describe the relaxation of small amplitude long wavelength inhomogeneities around a homogeneous state (swollen or shrunken) but it cannot account for the large volume changes that take place in some hydrogels. It does not contain an intrinsic driving force for the volume changes but this must be introduced through the initial condition which is thus different in the cases of swelling and shrinking. They are therefore appropriate to describe the response of the gel to a stimulus such as a change in solvent composition or temperature but they cannot describe swelling-deswelling cycles that have been observed in self-oscillating systems. Finally, as pointed out by Onuki (19), that diffusion equation overlooks the slow mode representing homogeneous swelling or shrinking with minor density inhomogeneities. It has also been criticized on other grounds (12, 20).

Relaxation methods provide a useful tool to probe the dynamical properties of physico-chemical systems. In this framework, the knowledge concerning how fast a gel shrinks or swells is essential for many technological applications. The relaxation time  $\tau$  of small perturbations about a steady state  $\phi_s$  is obtained by linearizing Eq. (8) to give

$$\tau = \frac{\phi_s^2}{\Gamma\phi_0 V_0} \left( \frac{\partial \Pi}{\partial \phi} \Big|_{\phi_s} \right)^{-1} = \frac{\phi_s^3}{\Gamma\phi_0 V_0 K}$$
(9)

The present dynamical description is thus compatible with the thermodynamic stability condition K>0.

From Eq. (9) we see that relaxation processes present a dramatic slowing down in the vicinity of instabilities such as critical or cloud points where  $K\rightarrow 0$ . The relaxation time indeed becomes infinitely large when the critical endpoint is approached both from above and from below. From Eq. (9) one can define a dynamical critical index  $\tau \propto |\chi - \chi_c|^{-n_c}$  with  $n_c = 2/3$ . Similarly, the transition rate (i.e. the inverse of the relaxation time) decreases when the final state to which the system is pumped comes close to the hysteresis limits ( $\chi_{sip} \phi_{si}$  with  $i \equiv$  c or s). This behavior  $\tau \propto |\chi - \chi_{si}|^{-n_s}$  can now be characterized by a spinodal index  $n_s = 1/2$ , according to Eq. (9). These phenomena of critical and spinodal slowing down have been experimentally observed on sub millimeter spherical NIPA gels (21, 22).

Finally, gels can also exhibit a slow relaxation when they are driven slightly outside the bistability region. More precisely, if the system is initially prepared in a state such that  $\phi_0 > \phi_{si}$  and  $\chi < \chi_{sc}$ , it undergoes a slowing down during its relaxation towards the swollen state when it is brought closer to the hysteresis limit ( $\chi_{sc}$ ,  $\phi_{sc}$ ). On this plateau (Figure 2), the system presents a slow power law decrease proportional to  $(\chi_{sc} - \chi)\tau_{pl}$ . The slope and the lifetime of this plateau are very sensitive to the proximity of the hysteresis limit  $\chi_{sc}$ . The lifetime is given by  $\tau_{pl} \propto \kappa (\chi - \chi_{sc})^{-1/2}$  where  $\kappa$  is a measure of the curvature of the hysteresis loop at the limit point. This dynamical behavior has also been experimentally observed during the swelling process of NIPA gels (22). After a



Figure 2. Relaxation curves slightly beyond the hysteresis limit  $\chi_{sc}$  for the same initial condition but for decreasing distance from the spinodal point.  $\alpha=1$ ,  $\beta=0.003$ ,  $\gamma=0.038$ ,  $\chi_{sc}=0.7233$ . (1) $\chi=0.723$  (2) $\chi=0.7232$  (3) $\chi=0.72322$ .

temperature jump, the gel starts at first to swell slowly until the process speeds up in the final stages. Both the inverse of the slope of the plateau and its lifetime are shown to diverge at the threshold. This mechanism can in principle show up both in the swelling and the shrinking processes. However as shown in Figure 1, the hysteresis loop in the gel systems is highly asymmetric. The curvature at the marginal stability limit of the collapsed state is smaller than at the other limit point. As a result at the same distance from the limit points the plateau lifetime is much larger and can thus more readily be observed in the swelling process. This phenomenon of spinodal slowing down presents generic features that only depend on the nature (saddle-node) bifurcation that delimit the domain of bistability and has for instance also been observed in chemical systems (23). It would thus be interesting to experimentally test the various scalings derived in this section.

## Self-oscillating gels

We now discuss the coupling between the swelling-deswelling dynamics as described above and a potentially oscillating chemical reaction. As chemical process we could have chosen realistic oscillating reactions that abound in the specialized literature such as, for instance, the Belousov-Zhabotinsky reaction or the bromate/sulfite/ferrocyanide pH oscillator (7). Kinetic schemes thereof may in some instances lead to semi-quantitative descriptions of the oscillations without resorting to the introduction of the ionic character of these reactions that occur in solutions. Nevertheless in this first approach and because the couplings with the gel have not yet been characterized we have chosen the formal Brusselator model that is known to exhibit autonomous oscillations that are well documented (24). For the ease of presentation, we therefore consider a neutral gel for which the discontinuous volume phase transition is induced by the dependence of the Flory interaction parameter on polymer volume fraction. We also suppose that some species involved in the reaction can influence the volume phase transition through the dependence of the expansion coefficients  $\chi_1, \chi_2, \chi_3$ ... on their concentrations. There lies the main coupling between the two subsystems. The governing kinetic equations then take the following form

$$\frac{d\phi}{dt} = -\Gamma \frac{\delta \Delta F(X, Y, \phi)}{\delta \phi}$$

$$\frac{dX}{dt} = f(X, Y) - \frac{X}{V} \frac{dV}{dt}$$

$$\frac{dY}{dt} = g(X, Y) - \frac{Y}{V} \frac{dV}{dt}$$
(10)

The model we explicitly consider is thus

$$\frac{d\phi}{dt} = \frac{\alpha}{\phi^2} \Big[ (1-\gamma)\phi + \ln(1-\phi) + \left(\chi_1^0 + \gamma_1 Y + \chi_2(2\phi-1)\right)\phi^2 + \beta\phi^{1/3} \Big]$$

$$\frac{dX}{dt} = A - (B+1)X + X^2Y + \frac{X}{\phi}\frac{d\phi}{dt}$$
(11)
$$\frac{dY}{dt} = BX - X^2Y + \frac{Y}{\phi}\frac{d\phi}{dt}$$

where the parameters  $\alpha$ ,  $\beta$  and  $\gamma$  have been defined earlier;  $\gamma_1$  describes the influence on the gel of Y, the sole species of the chemical reaction which changes the solvent properties through  $\chi_1 = \chi_1^0 + \gamma_1 Y$ ; A and B are chemical control parameters. In absence of phase transition chemical oscillations occur through a Hopf bifurcation at  $B_H = 1 + A^2$ . The last terms in the chemical kinetic equations are the concentration-dilution contributions taking into account the volume variations of the "gel reactor". The existence of these contributions

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imply that the role of chemistry is not, in general, merely that of a parametric forcing of the gel dynamics. We have a new dynamical system at hand.

Parameter space is thus multidimensional so that we only discuss some illustrative cases. For a first set of values of the parameters Figure 3 describes the



Figure 3. Bifurcation lines in the  $(\chi_2, B)$  plane of parameter space for  $\alpha = 0.2$ ,  $\beta = 0.00758$ ,  $\gamma = 0.00213$ ,  $\chi^0_1 = 0.3$ ,  $\gamma_2 = 0.32$ , A = 2. Plain lines are the locus of saddle-node bifurcations whereas the dotted lines are loci of Hopf bifurcations.

bifurcations in the  $(\chi_2, B)$  plane. Let us recall that  $\chi_2$  controls the size of the discontinuity of the volume phase transition in the absence of a chemical process while B is the standard bifurcation parameter of the Brusselator.

When  $\chi_2$  is sufficiently large, the swollen and collapsed states coexist for a range of values of B inside the cusped region. As a result of the coupling, each state can undergo a Hopf bifurcation leading to mechano-chemical oscillations. The loci of the bifurcations leading to these oscillations are represented by the foliated curve  $H_2H_3$  and the line  $H_1$  that remains near the value of  $B_H$  for the chosen values of the parameters. For these values, when  $\chi_2 = 1.02$ , the states of the polymer volume fraction are shown in Figure 4. For small values of B the swollen state (small value of  $\phi_s$ ) is stable and may eventually coexist with the shrunken state. However at H<sub>2</sub> the system undergoes a supercritical Hopf bifurcation to temporal oscillations. Meanwhile the collapsed state also undergoes a supercritical bifurcation at H<sub>1</sub>. The oscillations of the swollen state do not however persist as their stable limit cycle annihilates with an unstable limit cycle emanating from H<sub>3</sub>. For larger values of B only the oscillations of the shrunken state persist. The oscillations are of small amplitude as shown on Figure 5. There for small times we show the oscillations of the polymer volume fraction in the swollen state for B=6.5. After 20 units of time B is stepped up to 8 (beyond the collision of the stable and unstable limit cycles). The polymer



Figure 4. Polymer volume fraction  $\phi_s$  as a function of B. Solid and dotted lines respectively represent stable and unstable steady states. The parameters are as in Figure 3 and  $\chi_2 = 1.02$ .



Figure 5. Mechano-chemical oscillations and birhythmicity. Parameters as in Figure 3.

therefore shrinks as its volume fraction transits to oscillations around the upper branch. When the system has settled in this new state, at t = 80, *B* is then stepped down to 6.5 again. The polymer volume fraction keeps on oscillating around its shrunken state albeit with a smaller amplitude as one comes nearer the H<sub>1</sub> Hopf

In Nonlinear Dynamics in Polymeric Systems; Pojman, J., et al.; ACS Symposium Series; American Chemical Society: Washington, DC, 2003. bifurcation. This also shows that the system exhibits birhythmicity as, for instance at B = 6.5, oscillations around the swollen and collapsed state coexist.

Although it is difficult to be quantitative at this stage the smallness of the oscillations can be tracked to the relation between the characteristic time of the gel, related to  $\alpha$  and that of the chemistry. A measure of the last one is the inverse of the critical frequency of the limit cycle that is equal to A for the Brusselator. If this is so one may intuitively argue that when  $\alpha$  is too small or 1/A too large, chemistry "recalls" the gel before it has swollen or shrunken as much as it could. To test this we have measured the amplitude of the oscillations for the same conditions as before changing only the value of  $\alpha$ . The result is shown on Figure 6. Indeed the amplitude of the oscillations increase.



Figure 6. Influence of  $\alpha$  on the amplitude of the oscillations of  $\phi$  for B=8. Parameters as in Figure 3.

To show the reverse effect of varying A we have chosen somewhat different conditions where the critical point is embedded in the folium and the oscillations of the swollen state are more of a relaxation type. This is shown in Figure 7. The amplitudes of the oscillations increase as A decreases. It therefore seems that the product of the gel relaxation time  $\tau$  by the characteristic frequency  $\omega$  of the chemical oscillations,  $P = \omega \tau$ , provides the crucial parameter that determines the amplitude of these oscillations.

As illustrated in Figures 5 and 7 the amplitude and frequencies of the gel oscillations depend on the values of the chemical parameters. Figure 8 also shows that there is no phase shift in the oscillations of the chemical concentration and the polymer volume fraction. These effects has been observed in the recent experiments (4, 6, 25).

The fact that we are dealing with a new dynamical system is asserted by the fact that it may oscillate for reactant concentrations that are such that the chemical system on its own does not exhibit oscillations as it lies below its Hopf bifurcation limit.



Figure 7. Influence of A on the amplitude of the oscillations of  $\phi$  for B=0.026.  $\alpha$ =0.7,  $\beta$ =0.00758,  $\gamma$ =0.00213,  $\chi^0_1$ =0.5,  $\gamma_2$ =0.2.



Figure 8. In phase periodic oscillations of the polymer volume fraction around its shrunken state(dotted line) and the concentration of chemical species Y (plain line that represents Y/10).

## Conclusions

We have presented a very simple model that hints at how an oscillating chemical reaction can be used to drive the periodic oscillation of a piece of gel and thereby transduce chemical energy into mechanical work.

Our toy model however does not take into account the all important spatial effects originating from the diffusive properties of the matrix of the gel (and related to the elastic properties) and those of the reactive solute species. These will introduce further characteristic time scales and new length scales in the problem. The inclusion of such terms should allow for the description of the chemical waves observed by Yoshida et al (25).

In the absence of chemistry various approaches have been proposed to take such spatial effects into account (12, 18, 26, 27, 28, 29, 30, 31), but their relation to one another has not been tested thoroughly nor to what extend they include the spatial phenomena related to the volume phase transition as studied separately (19, 32). Along those lines a model for a sphere of gel presenting small temporal oscillations provoked by a stationary chemical reaction is presented in this volume with related experimental results (33).

The determination of the precise nature of the couplings between the reacting chemicals and the gel matrix, as well as their intensities should present interesting experimental and theoretical challenges.

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