

A model for self-oscillating miniaturized gels

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Introduction

It is well known that some polymer gels undergo large volume changes in response to external stimuli (temperature, solvent composition)¹. On the other hand, a large variety of chemical reactions have been shown to present autonomous oscillations under nonequilibrium conditions². Recently Yoshida and coworkers have reported the design of self-oscillating gels that exhibit spontaneous swelling-deswelling cycles by driving their mechanical properties with an oscillating chemical reaction³. It is the main purpose of this work to develop a simple theoretical model that describes some of the dynamical behaviors which can occur in such systems. It is based on a Landau-Khalatnikov equation for the polymer volume fraction coupled to the chemical kinetics. The coupling arises through the dependence of the volume phase transition on the concentration of some species involved in the chemical reaction. We have first verified that in absence of chemical reactions, this dynamical equation correctly reproduces the dramatic slowing-downs in the transition rates which have been observed in relaxation experiments near the critical point⁴ and the hysteresis limits⁵ of charged hydrogels.

In this paper, we study gels the dimensions of which are smaller than the characteristic wavelength of the chemo-elastic waves. This allows us to treat the gel as an homogeneous and isotropic nonlinear elastic medium in agreement with recent experiments performed on miniaturized gels⁶.

The volume phase transition

We first outline the thermodynamic theory of the volume phase transition of stimuli-responsive gels¹. The free energy is given as the sum of contributions due to mixing, elasticity and counter ions:

$$\Delta F = \Delta F_{mix} + \Delta F_{el} + \Delta F_{ion}. \quad (1)$$

The Flory-Huggins theory gives

$$\Delta F_{mix} = kTVv_1^{-1} \left[(1-\phi) \ln(1-\phi) + \chi\phi(1-\phi) \right] \quad (2)$$

where ϕ is the polymer volume fraction; V and v_1 are respectively the volume of the gel and the molar volume of the solvent. When it is only a function of temperature, the Flory interaction parameter χ is a convenient bifurcation parameter. On the basis of the simple rubber elasticity theory, ΔF_{el} can be expressed as

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

where V_0 and ϕ_0 are the volume and polymer volume fraction in the reference state and v_0 the cross link number density. Finally, ΔF_{ion} includes the translational entropy of the counter ions

$$\Delta F_{ion} = -kTV_0v_i \ln\left(\frac{\phi}{\phi_0}\right) \quad (4)$$

where v_i is the counter ion density.

The phases of the gel in equilibrium with the surrounding solvent are determined by the condition $\Pi(\phi) = 0$ where $\Pi(\phi)$ is the osmotic pressure

$$\Pi = -\left(\frac{\delta F}{\delta V}\right) = \frac{\phi}{V} \left(\frac{\delta F}{\delta \phi}\right) \quad (5)$$

As shown in Fig 1, a charged gel can undergo a volume phase transition by varying χ (i.e. the temperature). In principle, the transition takes place at $\chi = \chi_M$ where the free energy of the swollen state becomes equal to that of the collapsed state. However these systems generally exhibit an asymmetric hysteresis loop. As exhibited in **Figure 1** the temperature at which the collapse occurs is different from the threshold swelling temperature. Thermodynamic stability implies $K > 0$, where K is the bulk modulus defined by

$$K = \phi \left(\frac{\delta \Pi}{\delta \phi}\right)_T \quad (6)$$

The condition $K = 0$ determines the points χ_{sc} and χ_{ss} shown in **Figure 1**. They respectively correspond to the marginal stability limits of the collapsed and the swollen states. The locus of these points when the temperature or the solvent composition are varied forms the spinodal curve. The maximum of

this curve defines the critical point at which the volume phase transition becomes continuous⁴.

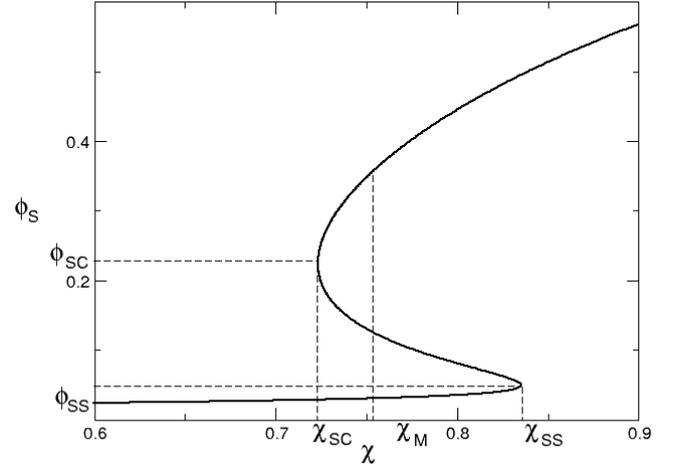


Figure 1. Equilibrium volume phase transition diagram for the gel. The polymer volume fraction ϕ is represented as a function of Flory's interaction parameter χ .

The polymer-solvent interaction parameter χ also depends on the polymer volume fraction. This can be taken into account by a power series expansion

$$\chi = \chi_1 + \chi_2\phi + \chi_3\phi^2 + \dots \quad (7)$$

It has been shown that a strong dependence on ϕ (i.e. a sufficiently large value of χ_2) can induce a discontinuous transition even in neutral gels⁷.

The polymer volume fraction plays the role of a non conserved order parameter. In homogeneous and isotropic gels, its time evolution is assumed to satisfy the following Landau-Khalatnikov equation

$$\frac{d\phi}{dt} = -\Gamma \left(\frac{\delta \Delta F}{\delta \phi}\right) = -\frac{\Gamma V_0 \phi_0}{\phi^2} \Pi \quad (8)$$

where the kinetic coefficient Γ fixes the time scale.

Because it explicitly takes into account the nonlinearities in the driving force for the phase transition, this description is better adapted to the description of the swelling-deswelling cycles than the classical theory based on a linear diffusion equation for the displacement field⁸.

Results and Discussion

Relaxation kinetics: The knowledge concerning how fast a gel shrinks or swells is essential for many technological applications. The relaxation time τ of small perturbations about a steady state ϕ_s is given by

$$\tau = \phi_s^3 / \Gamma \phi_0 V_0 K \quad (9)$$

From this equation, we see that the relaxation process presents 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 or below. From Eq. (9), one can define a dynamical critical index n_c such that

$\tau \propto |\chi - \chi_c|^{-n_c} \propto |T - T_c|^{-n_c}$ with $n_c = 2/3$. Similarly, the transition rate dramatically diminishes when the final state to which the system is jumped comes close to the hysteresis limits (χ_{si}, ϕ_{si} with $i = c$ or s); this behavior can now be characterized, from Eq. (9), by a spinodal index n_s as

$\tau_{si} \propto |\chi - \chi_{si}|^{-n_s}$, $n_s = 1/2$. Finally, gels exhibit an incubation period when they are driven slightly outside the bistability domain. More precisely, if the system is initially prepared in a state such that $\phi_o > \phi_{sc}$ and $\chi < \chi_{sc}$,

it undergoes a slowing down during its relaxation towards the swollen state when it comes close to the hysteresis limit (χ_{sc}, ϕ_{sc}) (plateau behavior). These phenomena have been experimentally observed in a series of sub millimeter charged gels^{4,5}. It would thus be interesting to experimentally check the various scaling laws 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. For the ease of presentation, we consider a neutral gel for which the discontinuous volume phase transition is induced by the dependence of the Flory interaction parameter on the volume fraction (cf. Eq. (7)). For the chemistry, we have chosen the Brusselator model that is known to exhibit autonomous oscillations. We also suppose that the concentration of some species involved in the reaction can shift the volume phase transition thresholds. This provides the main coupling between the two subsystems. The governing kinetic equations then take the following form

$$\begin{aligned} \frac{d\phi}{dt} &= \frac{\alpha}{\phi^2} \left[(1-\gamma)\phi + \ln(1-\phi) + (\chi_1 + \chi_2(2\phi-1) + \gamma_1 X + \gamma_2 Y)\phi^2 + \beta\phi^{\frac{1}{3}} \right] \\ \frac{dX}{dt} &= A - (B+1)X + X^2 Y + \frac{X}{\phi} \frac{d\phi}{dt} \\ \frac{dY}{dt} &= BX - X^2 Y + \frac{Y}{\phi} \frac{d\phi}{dt} \end{aligned} \quad (10)$$

where α , β and γ can be expressed in terms of the parameters appearing in ΔF ; γ_1 and γ_2 respectively describe the coupling with the activator X and the inhibitor Y of the chemical reaction; A and B are chemical control parameters. 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 imply that the role of chemistry is not simply that of a parametric forcing of the gel dynamics. We have a new dynamical system at hand.

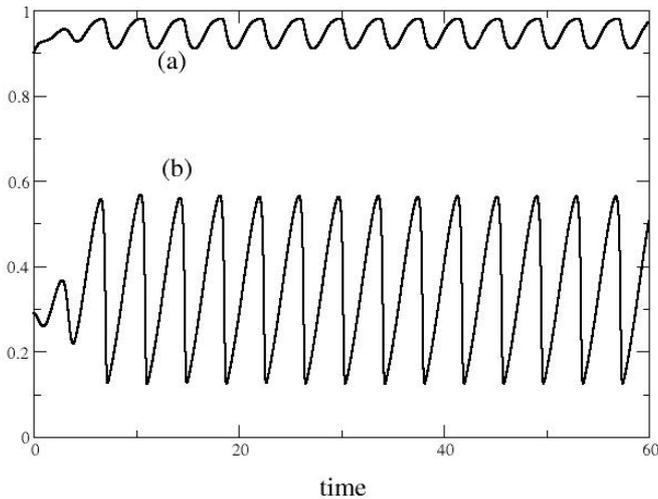


Figure 2. In phase periodic oscillations of the polymer volume fraction ϕ around its shrunken state (a) and the concentration of chemical species Y (b). The concentration Y has been divided by a factor 10.

When γ_2 is sufficiently large, the swollen and collapsed states coexist for a range of values of B . As a result of the coupling, each state can undergo a Hopf bifurcation leading to mechano-chemical oscillations. The product of the gel relaxation time τ by the characteristic frequency ω of the chemical oscillations, $P = \omega\tau$, provides the crucial parameter that determines the amplitude of these oscillations. When P is large, the system exhibits the phenomenon of birhythmicity. For a given value of the parameters, two different limit cycles coexist respectively centered on the collapsed and the swollen states. When P is decreased, one can observe large amplitude swelling-deswelling cycles. As illustrated in **Figure 2**, the chemical and mechanical oscillations are synchronized on the same period without a phase difference as in the recent experiments of Yoshida ⁶.

Conclusions

We have presented a simple model that describes how an oscillating reaction can be used to drive a self-oscillating gel and thereby produce mechanical work. This novel biomimetic material paves the way for a variety of promising technical and biomedical applications such as molecular motors, micropumps, new pacemakers, ... It would be interesting to include in the description the spatial effects (e.g. diffusion and shear modulus) in order to

account for the mechano-chemical waves that have also been observed in large systems.

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