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Kinetic modelling and bifurcation analysis of chemomechanically miniaturized gels under mechanical load

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Abstract. Chemomechanically responsive gels, with great potential applications in the fields of smart structures and biomedicines, present autonomously oscillatory deformation driven by the Belousov-Zhabotinsky chemical reaction. The dynamic behavior of the responsive gels is obviously affected by the external mechanical load. This approach proposed a kinetic model with an ordinary differential equation to describe the oscillatory deformation of the gels under the mechanical load. Then the periodic solutions and phase diagrams of the oscillation are obtained using the improved Runge-Kutta and shooting methods. The results demonstrated that bifurcations are typically existent in the system and the characters of the oscillatory deformation regularly depend on the mechanical load as well as the concentration of reactants and the stoichiometric coefficient of chemical reaction. This development is supposed to promote the practical applications of the chemomechanically responsive gels.

1 Introduction

Polymer gel is a complex network with long cross-linked polymers absorbing a lot of small molecules. Some synthetic gels are volumetrically sensitive to external stimulus, such as pH, temperature, light, and electric field [1–4]. These responsive gels generate periodic swelling-deswelling behaviors by rhythmically switching of the external stimulus and are developed as various functional devices (*e.g.*, actuators, sensors, and micro-valves) [5–7]. However, a recent development demonstrated that a gel presents an autonomous self-oscillation driven by the Belousov-Zhabotinsky chemical reaction (BZ reaction) [8]. The gel exhibits the unique capacity to transduce the chemical energy to the periodic deformation of the volume. This behavior is of particular interests because it is a hallmark of living organisms, for instance, the myocardial tissue similarly involves the conversion between chemical energy and mechanical action [9]. Recently, increasing attention is attracted on the related theories, experiments and applications [10–13].
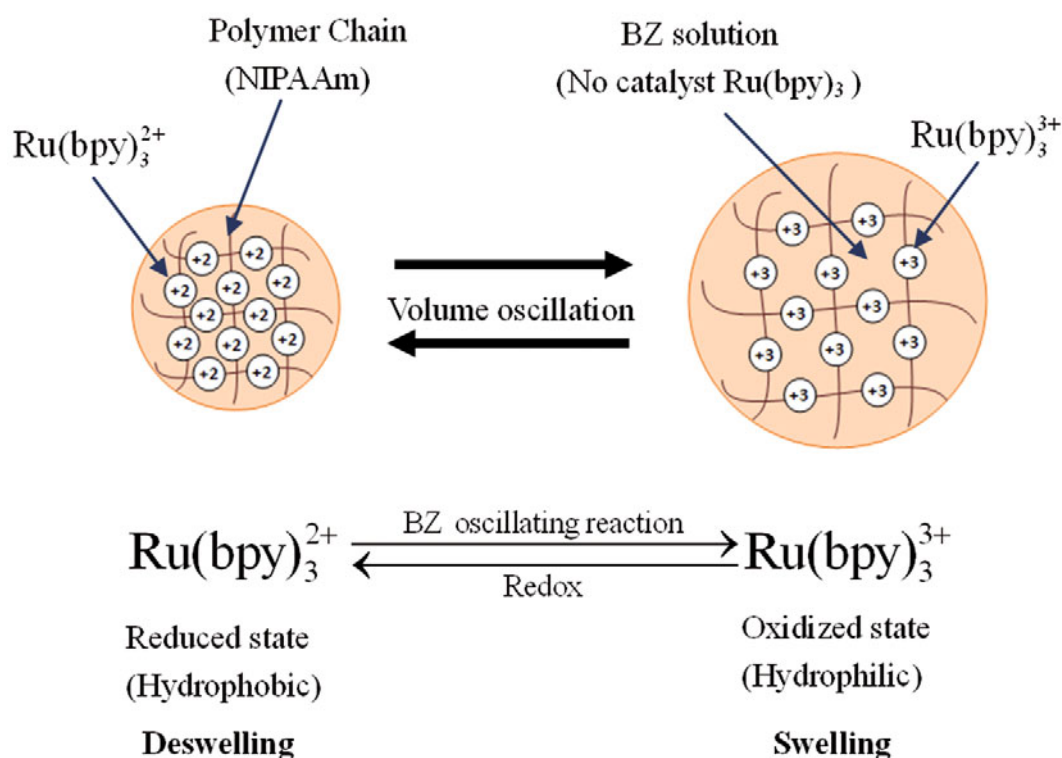
In the chemomechanically responsive gels, the reactive catalyst Ru(bpy)$_3$ is bonded on the polymer chains (fig. 1). The BZ reaction is activated while the gel with the fixed catalyst is immersed into the reactive solution without catalyst. During the BZ reaction, the fixed catalyst Ru(bpy)$_3$ periodically transforms between the oxidized state Ru(bpy)$_3^{3+}$ and the reduced state Ru(bpy)$_3^{2+}$, which induces periodic changes of the hydrophobicity of polymer chains and correspondingly results in the oscillatory deformation of the gel. Moreover, the characters of the oscillatory deformation greatly depend on the parameters of the chemical reaction, such as the concentration of reactants, stoichiometric coefficients, reaction rate constants and pH [14,15]. On the other hand, a recent experiment demonstrated the influence of mechanical force on the chemical reaction as well [16]. They resuscitated the BZ reaction and changed the characters of the reaction by applying a mechanical load on the gel. Consequently, the self-oscillation of the gel is a highly coupling process involving the large deformation of the gel and the complicated mechanism of chemical reaction, which gives considerable challenges to the related researches.

Fortunately, a series of admirable experiments have been done on the responsive gels and several significant devices have been invented using the smart materials [17, 18]. For instance, a soft robot, consisting of the smart

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Fig. 1. Schematic of the chemomechanically responsive gels driven by the Belousov-Zhabotinsky (BZ) reaction. The catalyst of BZ reaction, $Ru(bpy)_3$, is covalently bonded on the polymer chain and performs a redox process during the reaction, switching between the oxidized state and the reduced state. Different hydrophobicities of $Ru(bpy)_3^{2+}$ and $Ru(bpy)_3^{3+}$ result in the swelling and deswelling of the gel.

materials, is developed to walk on a platform like an insect [19]. Moreover, these smart materials are also adopted to make various structures of mass transport, biomimetic actuator and heart muscle [9,20]. All of the exploratory applications are designed as dynamic structures induced by the self-oscillation of the gel. Therefore, comprehensive analysis of the characters of the oscillatory deformation could greatly contribute to the practical applications of the materials.

Besides the experimental achievements, a number of related explorations have also been done in the field of theories [21–23]. The first reasonable model of the chemomechanically responsive gels is provided by Yashin and Balazs [24]. They coupled the deformation of the gel together with the kinetics of chemical reaction, investigated the trigger of chemical oscillation in a block of responsive gel induced by mechanical compression [25] and further probed the global response of localized mechanical impact in the gel [26]. It is worth noting that most of the studies focused on an inhomogeneous gel with a large size, in which pattern formation and propagation of chemical waves are observed in response to mechanical stimuli. These studies, using PDE equations with some specific system parameters to describe the chemical and mechanical evolution, are helpful to the application of self-oscillating gels in the field of signal transmission and energy transduction, etc. However, theoretical prediction of

the dynamic behavior of a miniaturized gel with homogeneously oscillatory deformation under a mechanical load is also very important for the application of self-oscillating gels as micro-actuator, micro-valve, etc.

As a related theory on a miniaturized gel, Suo *et al.* proposed another general model to describe large deformation of a responsive gel considering the diffusion of solvent in the gel, and comprehensively analyzed the influence of the mechanical load on the deformation and diffusion [27], which could be used to describe the mechanical behavior of a miniaturized gel. Unfortunately the model does not refer to the kinetics of the chemical reaction. Therefore, a modified kinetic model considering the externally mechanical load, deformation of the miniaturized gel and the kinetics of the chemical reaction is necessary to better uncover the coupling process between mechanics and chemistry.

For addressing the above objects, this paper proposed a modified model for the chemomechanically miniaturized gels under mechanical load. An ordinary differential equation (ODE) is obtained to describe the real-time state of the oscillatory deformation. Periodic solutions and phase diagrams of the self-oscillating process are probed. Finally, we demonstrated the influence of the mechanical load on the oscillating system by bifurcation analysis, which could contribute to the better understanding of the smart materials and the practical applications.
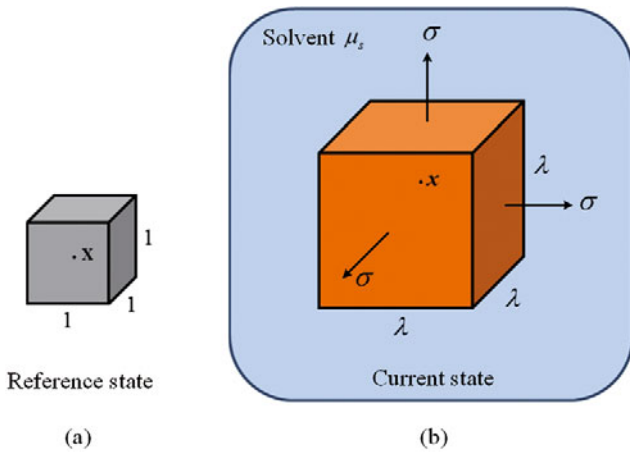
Fig. 2. Swelling of a gel with solvent diffusion and mechanical load. (a) Reference state: a unit cube of dry polymer network. **X** is the initial coordinate of a mark on the gel. (b) Current state: while immersing the dry network into solvent with chemical potential μ_s, the gel swells by the stretch of λ under the homogenously mechanical load σ. The mark moves to $\mathbf{x}(\mathbf{X}, t)$ due to the deformation of the gel.

2 Theoretical modeling

2.1 Mechanical equilibrium

To begin with the mechanical analysis (fig. 2), a unit cube of dry network is taken to be the reference state. For characterizing the deformation of the gel while immersing the dry network into solvent, a mark on the gel moving from the initial coordinates $\mathbf{X}$ to the current position $\mathbf{x}(\mathbf{X}, t)$ over a time t is described by the deformation gradient $\mathbf{F}$ with the components

$$F_{iK} = \frac{\partial x_i(\mathbf{X}, t)}{\partial X_K}, \quad i, K = 1, 2, 3. \tag{1}$$

After a period of homogenously swelling process by a stretch of λ, the gel obtains the mechanical equilibrium among the elastic stress of polymer, externally mechanical load σ_{ij} and the osmotic pressure of solvent with a chemical potential μ_s in the reservoir. Following the previous approach [28], the influence of solutes on the chemical potential of solvent is practically ignored while an ideally dilute solution is considered. Then the equation governing the mechanical equilibrium is given [27] (see appendix A)

$$\sigma_{ij} = \frac{\partial W}{\partial F_{iK}} \frac{F_{jK}}{\det(\mathbf{F})} - \frac{\mu_s}{\Omega} \delta_{ij}, \tag{2}$$

where, Ω is the volume of a molecule while δ_{ij} is a function defined as $\delta_{ij} = 1 (i = j)$ and $\delta_{ij} = 0 (i \neq j)$. The free energy of the gel W comes from two parts: stretching the network and mixing the polymers with solvent molecules, i.e., $W = W_{\text{net}} + W_{\text{mix}}$.

Based on Flory and Rechner's theories [29], the free energy of stretching the network is taken to be

$$W_{\text{net}} = \frac{1}{2} N k_B T [F_{iK} F_{iK} - 3 - 2 \log(\det(\mathbf{F}))], \tag{3}$$

where N is the number of polymer chains per volume in the reference state, k_B is the Boltzmann constant while T is the temperature of the system.

The free energy of mixing polymer chains with solvent molecules has been studied by Flory [30] and Huggins [31]. Considering the effect of the fixed metal-ion catalyst, the form of Flory-Huggins free energy of mixing is modified as

$$W_m = \frac{k_B T}{\Omega} \left[(\det(\mathbf{F}) - 1) \ln \left(1 - \frac{1}{\det(\mathbf{F})} \right) \right.$$
$$\left. + (\chi - \chi_v \cdot \Omega C_Z) \left(1 - \frac{1}{\det(\mathbf{F})} \right) \right]. \tag{4}$$

This contribution consists of the entropy of mixing the polymers and the solvent molecules, and the enthalpy of mixing with a dimensionless parameter χ. In addition, the influence of the catalyst bonded on the polymer chains of the responsive gel is especially considered here, which contributes to the enthalpy of mixing through changing the hydrophobicity of the polymer chains. The dimensionless variable ΩC_Z is the total volume of the catalyst molecules Ru(bpy)_3^{3+} in the reaction and χ_v is the related parameter, i.e., the enthalpy of mixing also depends on the quantity of Ru(bpy)_3^{3+}. Then the deformation of the gel is linked with the oscillating chemical reaction by the item $\chi_v \cdot \Omega C_Z$.

Recalling that the volume fraction of polymer chains in a gel relates to the deformation gradient by $\phi = 1 / \det(\mathbf{F})$ and setting a homogenously mechanical load $\sigma_1 = \sigma_2 = \sigma_3 = \sigma$ (e.g., hydrostatic pressure) and the chemical potential of solvent in the reservoir $\mu_S = 0$ in eq. (2), correspondingly, eq. (2), together with eqs. (3) and (4), is specified as
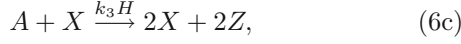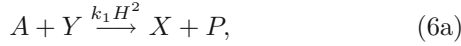
$$\sigma = N k_B T (\phi^{1/3} - \phi)$$
$$+ \frac{k_B T}{\Omega} [\ln(1 - \phi) + \phi + \chi \phi^2 - \chi_v v \phi], \tag{5}$$

where the true concentration of the fixed catalyst in the current state v relates to the number of catalyst molecules by $v = \Omega C_Z / \det(\mathbf{F})$. The first item on the right-hand side of eq. (5) describes the elastic stress of polymer chains while the last item is related to the osmotic pressure. Here, we mainly consider the oscillatory deformation of a sufficiently small gel, which means that the diffusion of the solvent is very fast comparing with the process of chemical reaction and the system obtains mechanical equilibrium instantaneously during the chemical reaction. When the gel swells freely without any constraint, i.e., $\sigma = 0$, the elastic stress of polymer chains and the osmotic pressure of the solvent reach mutual equilibrium and then eq. (5) is reduced to be similar to the model mentioned in the literature [15].

2.2 Kinetics of reaction and diffusion

To describe the BZ reaction, Field et al. developed the Field-Körös-Noyes (FKN) mechanism and gave the Oregonator model to describe the mechanism, including five

reactions [32]

$$A + Y \xrightarrow{k_1 H^2} X + P, \tag{6a}$$

$$X + Y \xrightarrow{k_2 H} 2P, \tag{6b}$$

$$A + X \xrightarrow{k_3 H} 2X + 2Z, \tag{6c}$$

$$2X \xrightarrow{k_4} A + P, \tag{6d}$$

$$B + Z \xrightarrow{k_5} \frac{1}{2} fY, \tag{6e}$$

where $A = [\mathrm{BrO_3^-}]$, $B = [\text{oxidizable species}]$, $P = [\mathrm{HOBr}]$, $H = [\mathrm{H^+}]$, $X = [\mathrm{HBrO_2}]$, $Y = [\mathrm{Br^-}]$ and $Z = [M_{\mathrm{ox}}]$. k_1, k_2, k_3, k_4, k_5 are, respectively, the reaction rate constants of each reaction. The stoichiometric coefficient f represents the number of $\mathrm{Br^-}$ produced by the reduction of two molecules of M_{ox}, which is changeable for the oscillating reactions with different catalysts including $\mathrm{Ce^{4+}}$, $\mathrm{Fe(phen)_3^{3+}}$ and $\mathrm{Ru(bpy)_3^{3+}}$. Moreover, f, also related to the temperature and pH, is supposed to be larger than 0.5 in an oscillating reaction [33]. For the chemomechanically responsive gels, the characters of the chemical reaction and the deformation of the gel obviously depend on the parameter f.

The Oregonator model treats the concentration of reactants A, B, P, H as constants while X, Y, Z are treated as changeable intermediates. Considering that the concentration of Y changes much faster than X and Z, it is assumed that $\frac{\mathrm{d}Y}{\mathrm{d}t} \equiv 0$. Therefore, kinetics of the chemical reaction could be described with only two variables X and Z. The dimensionless concentration variables $u = \frac{X}{X_0}$, $v = \frac{Z}{Z_0}$ are adopted for the following theoretical analysis, where X_0, Z_0 are the reference concentrations.

According to the law of mass conservation, the changes of the concentration of reactants mainly consist of two parts: chemical reaction and diffusion, namely

$$\frac{\mathrm{d}\boldsymbol{c}}{\mathrm{d}t} = \left(\frac{\mathrm{d}\boldsymbol{c}}{\mathrm{d}t}\right)_R + \left(\frac{\mathrm{d}\boldsymbol{c}}{\mathrm{d}t}\right)_D, \quad \boldsymbol{c} = \begin{bmatrix} u \\ v \end{bmatrix}, \tag{7}$$

where, $\left(\frac{\mathrm{d}\boldsymbol{c}}{\mathrm{d}t}\right)_R$ represents the concentration changes induced by the chemical reaction while $\left(\frac{\mathrm{d}\boldsymbol{c}}{\mathrm{d}t}\right)_D$ represents the concentration changes induced by diffusion.

In this paper, the volume fraction of polymers ϕ is a variable to describe the volume changes of the gel. Considering the influence of polymer network on the concentration of reactants [15,28], the concentration changes of the two intermediates caused by the chemical reaction are given as

$$\left(\frac{\mathrm{d}\boldsymbol{c}}{\mathrm{d}t}\right)_R = \begin{bmatrix} F(u,v,\phi) \\ \varepsilon G(u,v,\phi) \end{bmatrix}, \tag{8}$$

where

$$F(u,v,\phi) = (1-\phi)^2 u - u^2 - (1-\phi)fv\frac{u - q(1-\phi)^2}{u + q(1-\phi)^2}, \tag{9}$$

$$G(u,v,\phi) = (1-\phi)^2 u - (1-\phi)v. \tag{10}$$

In the above equations, the dimensionless parameters ε and q are related to the initial concentration of reactants

and reaction rate constants, namely

$$\varepsilon = \frac{k_5 B}{k_3 H A}, \quad q = \frac{2k_1 k_4}{k_2 k_3}. \tag{11}$$

While the gel keeps an oscillatory deformation due to the chemical reaction, the reactants in the gel diffuse together with the solvent. The equation of diffusion could be written as [15]

$$\left(\frac{\mathrm{d}\boldsymbol{c}}{\mathrm{d}t}\right)_D = \begin{bmatrix} -u(1-\phi)^{-1}\frac{\mathrm{d}\phi}{\mathrm{d}t} \\ v\phi^{-1}\frac{\mathrm{d}\phi}{\mathrm{d}t} \end{bmatrix} \tag{12}$$

2.3 State equations of the gel

To probe the real-time state of the responsive gel, a state variable $y = \begin{bmatrix} \phi \\ \dot{\phi} \end{bmatrix}$ is defined to describe the oscillatory deformation. According to the theories of nonlinear dynamics, ϕ is the generalized displacement of the gel while $\dot{\phi}$ is the generalized velocity, $i.e.$, $\dot{\phi} = \mathrm{d}\phi/\mathrm{d}t$. Correspondingly, the governing equation of the state variable could be derived from the condition of mechanical equilibrium eq. (5) and the kinetics of reaction and diffusion eq. (7).

The variable v in eq. (5) is reformulated as a function of ϕ, namely

$$v(\phi) = \frac{1}{\chi_v}\left\{ -\frac{\sigma\Omega}{k_B T}\cdot\frac{1}{\phi} + \Omega N(\phi^{-2/3} - 1) \right.$$
$$\left. + \left[\frac{\ln(1-\phi)}{\phi} + 1 + \chi\phi\right] \right\}. \tag{13}$$

Substituting eqs. (8)-(10) and (12) into eq. (7), together with eq. (13), gives the governing equations of the oscillatory deformation in the form

$$\dot{y} = \mathrm{d}\begin{bmatrix} \phi \\ \dot{\phi} \end{bmatrix}\bigg/\mathrm{d}t$$
$$= \begin{bmatrix} \dot{\phi} \\ \frac{F(\phi,\dot{\phi})}{A(\phi)} - \frac{v'(\phi)(1-\phi)+2v(\phi)}{(1-\phi)^2 A(\phi)}\dot{\phi} - \left[\frac{1}{1-\phi} + \frac{A'(\phi)}{A(\phi)}\right]\dot{\phi}^2 \end{bmatrix}, \tag{14}$$
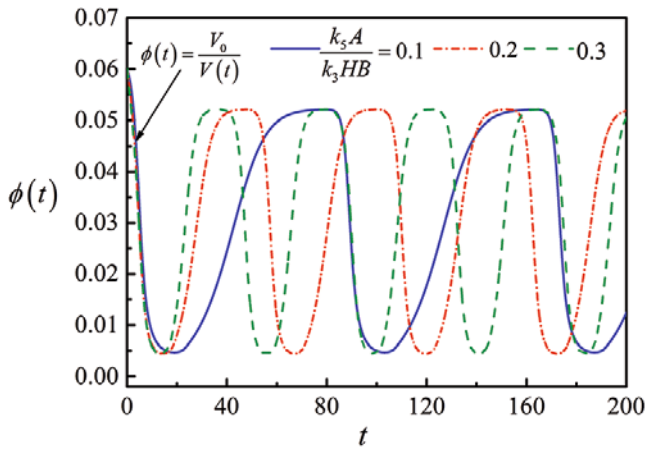
where

$$A(\phi) = \frac{h(\phi)/\chi_v - v(\phi)/\phi}{\varepsilon(1-\phi)^2}, \tag{15}$$

$$h(\phi) = \frac{\sigma\Omega}{k_B T}\frac{1}{\phi^2} - \frac{2}{3}N\Omega\phi^{-\frac{5}{3}}$$
$$- \frac{\ln(1-\phi)}{\phi^2} - \frac{1}{\phi(1-\phi)} + \chi. \tag{16}$$

$A'(\phi)$ in eq. (14) is the derivative of eq. (15), $i.e.$, $A'(\phi) = \mathrm{d}A(\phi)/\mathrm{d}\phi$, while similarly $v'(\phi)$ is the derivative of eq. (13). In addition, $F(\phi,\dot{\phi})$ in eq. (14) is the reformulation of eq. (9) where the variables u and v are replaced by the functions of ϕ and $\dot{\phi}$. Besides the expression of v in

Fig. 3. Oscillatory deformation of the gel. The volume fraction of polymers $\phi(t)$ is related to the current volume of the gel $V(t)$ and the initial volume of the dry polymers in the reference state V_0. The character of oscillation depends on the dimensionless concentration of reactants ε (*i.e.*, $\varepsilon = \frac{k_5 A}{k_3 HB}$), with different values of 0.1, 0.2, 0.3. The other constant dimensionless parameters: $f = 0.7$, $\chi_v = 0.105$ and $-\frac{\sigma \Omega}{k_B T} = 0$.

eq. (13), the variable u derives from the second component of eq. (7) with the expression

$$u = A(\phi)\dot{\phi} + \frac{v}{(1 - \phi)}. \tag{17}$$

Accordingly, the governing ordinary differential equation (14), only involving the variable ϕ, presents the kinetic model for studying the dynamic behaviors of the oscillatory deformation of the gel.

2.4 Periodic solutions

The improved Runge-Kutta numerical method [34] with changeable steps is adopted to solve eq. (14). Figure 3 gives the simulation of the oscillatory deformation and shows the influence of the dimensionless concentration of reactants ε (*i.e.*, $\varepsilon = \frac{k_5 B}{k_3 HA}$) on the characters of oscillation while the other parameters are kept constant, such as the dimensionless mechanical load $-\frac{\sigma \Omega}{k_B T} = 0$, $\chi_v = 0.105$ and $f = 0.7$ while the initial value of ϕ is selected as 0.06. Additionally, fig. 3 suggests that the dynamic process of the gel tends to a periodic oscillation and the frequency is visibly changeable depending on the concentration of reactants, but the amplitude of deformation changes slightly. In order to further analyze the state of the gel, the periodic solution of the oscillation is also obtained by adopting an improved shooting method [35]: assuming $y(0) - y(T) = 0$ (T is the dimensionless period), the periodic solution of oscillation is converted to the boundary value problem of the ordinary differential equation (14) and then the boundary value problem is solved by using the Newton-Raphson method [36].
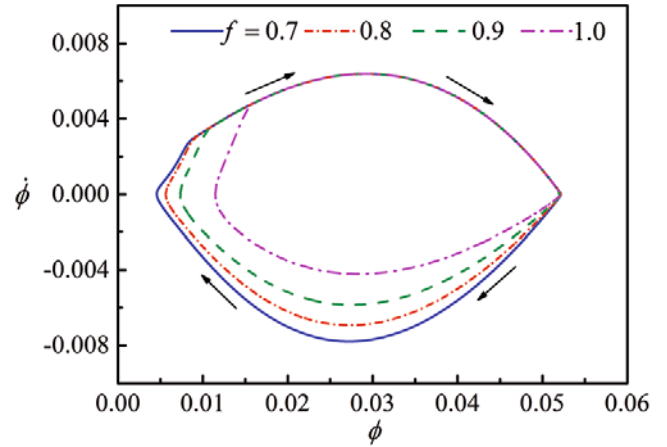

Fig. 4. Phase diagrams of the limit-cycle oscillation of the gel. The changing rate of the volume fraction of polymers $\dot{\phi}$ is plotted with respect to the volume fraction ϕ. The stoichiometric coefficient f of the BZ reaction depends on the type of catalyst, pH and temperature. The other constant dimensionless parameters: $f = 0.7$, $\varepsilon = 0.354$ and $-\frac{\sigma \Omega}{k_B T} = 0$.

3 Results and discussion

3.1 State analysis of a free gel

In the phase space of the oscillatory deformation of a free gel without any mechanical load, we obtained the phase diagrams of limit-cycle oscillations plotting the generalized velocity of the gel $\dot{\phi}$ with respect to the generalized displacement ϕ within a period solved by the shooting method (fig. 4). Each cycle represents the periodic solution of the oscillatory deformation with different values of the stoichiometric coefficient f, *i.e.*, the state diagrams of the gel depend on several factors, such as the type of catalyst, temperature and pH. Here, taking the cycle with $f = 0.7$ as an example, ϕ changes between 0.004 and 0.054 while $\dot{\phi}$ changes between -0.008 and 0.005. Meanwhile, fig. 4 shows that the domain of the limit-cycle becomes narrow while f increases, *i.e.*, changing the stoichiometric coefficient results in different patterns of oscillatory deformation of the gel. Moreover, the maximum values of ϕ rarely change while the minimum values of ϕ are various, *i.e.*, different values of f only change the maximum volume of the gel. When the other parameters are kept constant ($-\frac{\sigma \Omega}{k_B T} = 0$, $\chi_v = 0.105$ and $\varepsilon = 0.354$) and f is sufficiently large, it is predicted that the limit-cycles shrink toward the stable point $(0.054, 0)$. A deductive reason for this phenomenon is that a bigger value of f means a higher catalytic efficiency of the fixed catalysts, and consequently less catalysts are needed to periodically transform between the states of $Ru(bpy)_3^{3+}$ and $Ru(bpy)_3^{3+}$ while the redundant catalysts consistently maintain the state of $Ru(bpy)_3^{2+}$. In a prepared responsive gel, the total number of $Ru(bpy)_3^{3+}$ and $Ru(bpy)_3^{2+}$ is constant. The maximum values of ϕ (*i.e.*, the minimum volume of the gel) depend on the numbers of $Ru(bpy)_3^{2+}$ and rarely change because all of $Ru(bpy)_3$ have been in the state of $Ru(bpy)_3^{2+}$
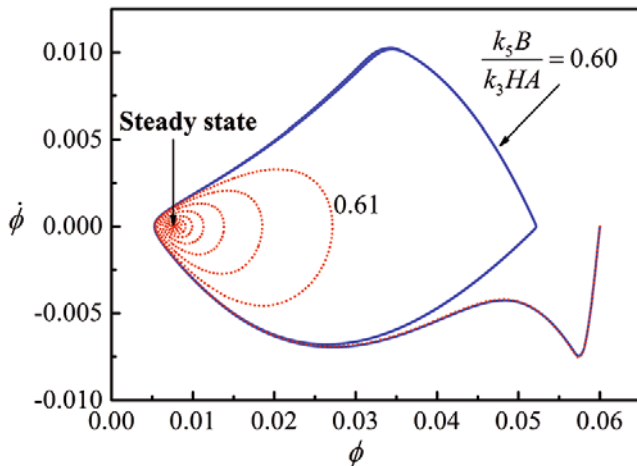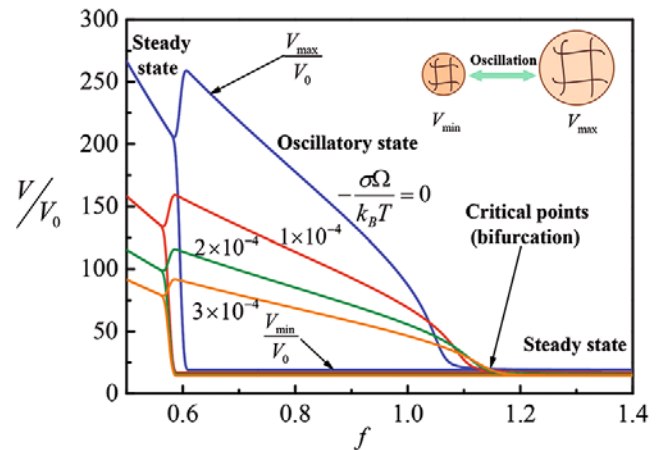
Fig. 5. Sensitivity of the dynamic behavior of the gel. With the same initial values of volume fraction, $\phi(0) = 0.06$, and system parameters ($-\frac{\sigma\Omega}{k_B T} = 0$, $\chi_v = 0.105$ and $f = 0.7$), the gel maintains a periodic deformation while $\varepsilon = 0.60$, but tends to a steady state while $\varepsilon = 0.61$.

Fig. 6. f-related bifurcations of the state of the gel. Undergoing a dimensionless mechanical load $-\frac{\sigma\Omega}{k_B T}$, the volume changes of the gel, V/V_0, is plotted as a function of the stoichiometric coefficient f. For each curve with different mechanical loads (0, 0.0001, 0.0002, 0.0003), the maximum volume $V_{\max}$ and minimum volume $V_{\min}$ of the gel are different in the middle section (*i.e.*, approximately $0.6 < f < 1.1$), which means that the gel maintains a periodic deformation (oscillatory state). Differently, the maximum volume and the minimum volume merge together while f is sufficiently small or large (*i.e.*, approximately $f < 0.6$ or $f > 1.1$), which indicates that no oscillation exists in this area (steady state). In addition, $\varepsilon = 0.354$; $\chi = 0.105$.

when Ru(bpy)$_3^{3+}$ are completely reduced to the state of Ru(bpy)$_3^{2+}$ at the stable point of the cycles (0.054, 0). Differently, the maximum number of Ru(bpy)$_3^{3+}$ presenting in the reaction depends on f and affects the minimum value of ϕ. For instance, more Ru(bpy)$_3^{2+}$ are activated to participate in the redox process and transform to the state of Ru(bpy)$_3^{3+}$ if f is small.

Besides the influence of the stoichiometric coefficient, the state of the gel is also sensitive to the dimensionless parameter ε, which is related to the concentration of reactants and reaction rate constants. Here, we investigated two phase diagrams of the gel with slightly different values of ε, as shown in fig. 5. The gel with $\varepsilon = 0.60$ shows a limit-cycle oscillation while the gel with $\varepsilon = 0.61$ tends to a steady state. The initial value for these simulation is uniformly selected as $\phi(0) = 0.06$.

## 3.2 State analysis of a constrained gel

Being different from the phase diagrams of the free gel, bifurcation, a unique phenomenon in the nonlinear dynamic system, is analyzed to further uncover the state changes of the constrained gel with a mechanical load. Figure 6 gives a series of bifurcations under different mechanical loads and shows the state changes of the gel depending on f. Recalling the relation among the current volume of the gel V, the initial volume of dry polymers V_0 and the volume fraction of polymers ϕ as $\frac{V}{V_0} = \frac{1}{\phi}$, we used the current volume to analyze the bifurcations of the gel in this section. If there is no mechanical load, *i.e.*, the dimensionless parameter $-\frac{\sigma\Omega}{k_B T} = 0$ (fig. 6, blue line), the gel presents a steady state with a sufficiently large or small values of f but the volumes of the steady states are various. When f locates in the middle range (*i.e.*, approximately $0.6 < f < 1.1$), the gel maintains a continuous oscillation between the maximum volume and the minimum volume.

If there is a mechanical load applying on the gel, the maximum volume of the oscillatory state of the gel decreases with the mechanical load increasing ($-\frac{\sigma\Omega}{k_B T} = 1 \times 10^{-4}, 2 \times 10^{-4}, 3 \times 10^{-4}$). Meanwhile, the amplitudes of oscillatory deformation get smaller and, on the opposite, the range of f for the continuous oscillation becomes a little bigger.

In addition to the influence of a mechanical load on the f-related bifurcations, we also analyzed the bifurcations with respect to the concentration of reactants under a mechanical load, because the concentration of reactants is a much easier factor to control within the application of the responsive gel. Figure 7 presents the bifurcations of the constrained gel depending on ε. It is obvious that the gel exhibits oscillatory deformation while ε is smaller than the critical value and keeps in a steady state once ε exceeds the critical value. What is more important is the influence of mechanical load on the bifurcations. The amplitudes of the oscillatory deformation decrease with the mechanical load increasing and meanwhile the critical value of ε obviously becomes larger. Interestingly, within a certain range of the concentration of reactants (*i.e.*, approximately $0.6 < \varepsilon < 0.7$), the state of the gel is uniquely sensitive to the mechanical load, *i.e.*, the state of the gel could transform from a steady state to an oscillatory state while the mechanical load increases but the other parameters are kept constant, which indicates a potential application of the gel as a force-sensor.
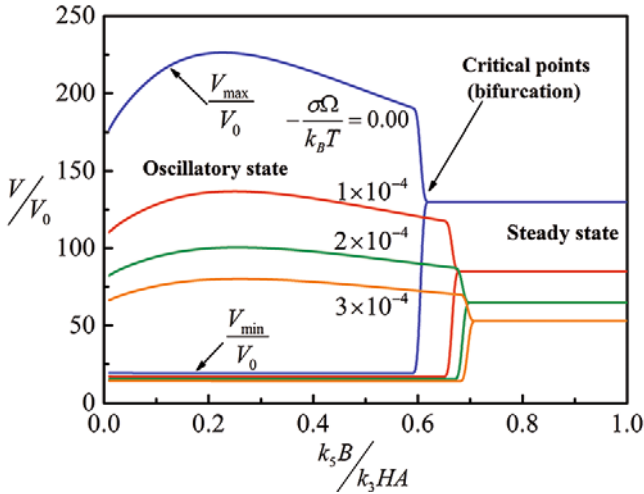
Fig. 7. ε-related bifurcations of the state of the gel. In the left part of each curve with different mechanical loads (*i.e.*, $-\frac{\sigma\Omega}{k_BT} = 0$, 0.0001, 0.0002, 0.0003), different values of $V_{\max}$ and $V_{\min}$ indicate the oscillatory state of the gel. While ε is larger than the critical points, the gel comes into a steady state. Here, $f = 0.7$; $\chi = 0.105$.

4 Remarks

Coupling the thermodynamics of the gel and kinetics of reaction and diffusion, this paper developed a kinetic model to describe the dynamic behaviors of chemomechanically miniaturized gels under mechanical load. The oscillatory deformation of the gel is theoretically governed by an ordinary differential equation (ODE). State analysis, based on the solution of the ODE by improved Runge-Kutta and shooting numerical methods, suggests that the gel presents a periodically oscillatory deformation with the form of limit-cycle pattern in the phase diagrams, but the gel tends to a steady state while the parameters of the system (*e.g.*, the stoichiometric coefficient and reactant concentration) locate in the improper ranges. Additionally, the diagrams of bifurcations further suggest that the state of the gel visibly depends on the mechanical load as well as the parameters of the system, *i.e.*, the characters of the oscillatory deformation and the critical points of bifurcations are obviously affected by the mechanical load. These results may be helpful to the inventive insights of the practical applications of the smart materials.

Appendix A.

Appendix A.1. Mechanical equilibrium: eqs. (2) and (5)

Thermodynamics dictates that the Helmholtz free energy (G) of the system should never increase, namely

$$\delta G \leq 0. \tag{A.1}$$

The inequality holds when the system is not in equilibrium, and the equality holds when the system is in equilibrium.

The change of Helmholtz free energy of the system is the sum over the parts: the free energy (W) in the gel, the free energy in the external solution, and the mechanical force doing work, namely

$$\delta G = \delta W - \mu_s \delta C - s_{iK} \delta F_{iK}. \tag{A.2}$$

μ_s is the chemical potential in the reservoir while C is the number of solvent molecules in the gel. s_{iK} is the component of normal stress applied on the gel. F_{iK} is the component of deformation gradient **F**. The Helmholtz free energy of the gel is taken to be a function of the deformation gradient and the number of solvent molecules

$$W = W(\mathbf{F}, C). \tag{A.3}$$

Taking a unit cube of dry polymers as a reference state, we assume that individual polymers and solvent molecules are incompressible, namely

$$1 + \Omega C = \det(\mathbf{F}), \tag{A.4}$$

where, Ω is the volume of a molecule.

The condition of incompressibility indicates that C and F_{iK} are not independent variables in eqs. (A.2) and (A.3). According to differential calculus, when the gel absorbs a number of solvent molecules and deforms by δF_{iK}, the free energy of the gel changes by

$$\delta W = \frac{\partial W}{\partial F_{iK}} \delta F_{iK}. \tag{A.5}$$

Recalling the relation $\partial \det(\mathbf{F})/\partial F_{iK} = H_{iK} \det(\mathbf{F})$, eq. (A.4) gives

$$\delta C = \frac{1}{\Omega} H_{iK} \det(\mathbf{F}) \delta F_{iK}. \tag{A.6}$$

Together with (A.5) and (A.6), (A.2) becomes

$$\delta G = \left[\frac{\partial W}{\partial F_{iK}} - \frac{\mu_s}{\Omega} H_{iK} \det(F) - s_{iK} \right] \delta F_{iK}. \tag{A.7}$$

The system is always considered in the state of thermodynamic equilibrium. According to eq. (A.1) and eq. (A.7), we obtain

$$s_{iK} = \frac{\partial W}{\partial F_{iK}} - \frac{\mu_s}{\Omega} H_{iK} \det(F). \tag{A.8}$$

Considering that the true stress relates to the nominal stress by $\sigma_{ij} = s_{iK}F_{jK}/\det(\mathbf{F})$ and the definition $H_{iK}H_{jK} = \delta_{ij}$, the equation governing the mechanical equilibrium is given as

$$\sigma_{ij} = \frac{\partial W}{\partial F_{iK}}\frac{F_{jK}}{\det(\mathbf{F})} - \frac{\mu_s}{\Omega}\delta_{ij}, \qquad (A.9)$$

where δ_{ij} is a function defined as $\delta_{ij} = 1(i = j)$ and $\delta_{ij} = 0(i \neq j)$.

The free energy of the gel W comes from two parts: stretching the network and mixing the polymers with solvent molecules, *i.e.*, $W = W_{\text{net}} + W_{\text{mix}}$, which is given as eqs. (3) and (4).

Together with eqs. (3) and (4), eq. (A.9) is specified as

$$\sigma_{ij} = Nk_BT\left[\frac{F_{iK}F_{jK}}{\det(\mathbf{F})} - \frac{\delta_{ij}}{\det(\mathbf{F})}\right] + \frac{k_BT}{\Omega}$$
$$\times \left[\begin{array}{l}\ln\left(1 - \frac{1}{\det(\mathbf{F})}\right) + \frac{1}{\det(\mathbf{F})} + \\ (\chi - \chi_v \cdot \Omega C_Z)\frac{1}{\det(\mathbf{F})}\frac{1}{\det(\mathbf{F})}\end{array}\right]$$
$$\times \delta_{ij} - \frac{\mu_s}{\Omega}\delta_{ij}. \qquad (A.10)$$

Recalling that the volume fraction of polymer chains in a gel relates to the deformation gradient by $\phi = 1/\det(\mathbf{F})$ and setting a homogenously mechanical load $\sigma_1 = \sigma_2 = \sigma_3 = \sigma$ (*e.g.*, hydrostatic pressure) and the chemical potential of the solvent in the reservoir $\mu_S = 0$ in eq. (A.9), correspondingly, eq. (A.10) is simplified as eq. (5).

Appendix A.2. State equation: eq. (14)

The derivative of eq. (13) is

$$\frac{\mathrm{d}v}{\mathrm{d}t} = \frac{h(\phi)}{\chi_v}\frac{\mathrm{d}\phi}{\mathrm{d}t}, \qquad (A.11)$$

where $h(\phi)$ is given as eq. (16).

Combining eq. (A.11) and the expression of $\mathrm{d}v/\mathrm{d}t$ in eq. (7), the variable u is solved as a function of v and ϕ, namely

$$u = A(\phi)\frac{\mathrm{d}\phi}{\mathrm{d}t} + \frac{v}{(1-\phi)}, \qquad (A.12)$$

where $A(\phi)$ is given in eq. (15).

Consequently, the derivative of u gives

$$\frac{\mathrm{d}u}{\mathrm{d}t} = A'(\phi)\left(\frac{\mathrm{d}\phi}{\mathrm{d}t}\right)^2 + A(\phi)\frac{\mathrm{d}^2\phi}{\mathrm{d}t^2}$$
$$+ \frac{v'(\phi)(1-\phi) + v(\phi)}{(1-\phi)^2}\frac{\mathrm{d}\phi}{\mathrm{d}t}, \qquad (A.13)$$

where $A'(\phi)$ is the derivative of $A(\phi)$, *i.e.*, $A'(\phi) = \mathrm{d}A(\phi)/\mathrm{d}\phi$, while similarly $v'(\phi)$ is the derivative of $v(\phi)$ in eq. (13).

By eliminating $\mathrm{d}u/\mathrm{d}t$ in eqs. (A.13) and (7), the state equation of ϕ is given as

$$\frac{\mathrm{d}^2\phi}{\mathrm{d}t^2} = \frac{F\left(\phi, \frac{\mathrm{d}\phi}{\mathrm{d}t}\right)}{A(\phi)} - \left[\frac{A'(\phi)}{A(\phi)} - \frac{1}{1-\phi}\right]\left(\frac{\mathrm{d}\phi}{\mathrm{d}t}\right)^2$$
$$- \frac{v'(\phi)(1-\phi) + 2v(\phi)}{(1-\phi)^2}\frac{\mathrm{d}\phi}{\mathrm{d}t}. \qquad (A.14)$$

According to the theories of dynamics, the governing equation (A.14) is reformulated as eq. (14).

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