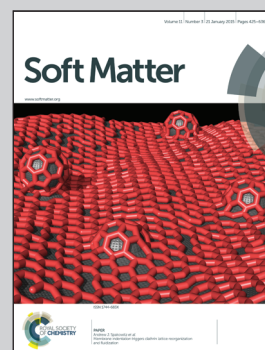


Highlighting work from Bioinspired Engineering and Biomechanics Center (BEBC), Xi'an Jiaotong University, Xi'an, China.

Title: Reaction-induced swelling of ionic gels

A chemomechanical theory is proposed to describe the dynamic behavior and response time of ionic gels driven by a common non-equilibrium chemical reaction. The dynamic deformation and response time of an ionic gel are dependent on the concentration of reactive and non-reactive ions, the time of exposure to external stimuli, the initial state and the density of ionizable groups on the polymer chains.

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Reaction-induced swelling of ionic gels[†]

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A chemomechanical theory is proposed to describe the dynamic behavior and response time of ionic gels. The large deformation of these gels accompanied by the migration of mobile ions is driven by a common non-equilibrium chemical reaction. The theoretical model was validated using existing experimental data. Further investigations showed that the dynamic deformation and response time of an ionic gel are dependent on the concentration of reactive and non-reactive ions, the time of exposure to external stimuli, the initial state and the density of ionizable groups on the polymer chains.

1. Introduction

Ionic gels consist of ionic polymers and a solution. These gels exhibit large amounts of deformation in response to mechanical forces,^{1,2} changes in temperature^{3–5} and pH,⁶ light^{7–9} and electrical^{10,11} and magnetic¹² fields. Natural ionic gels in the periphery of plant and animal cells have important roles in the regulation of water and in stabilizing the shape of cells.^{13,14} Synthetic ionic gels have been widely used in engineering as environmental sensors,¹⁵ biomimetic actuators,¹⁶ in autonomous flow control⁶ and in drug delivery systems.^{12,17} In these applications, the dynamic characteristics of ionic gels are important in device performance and improvements in the response time of devices based on ionic gels has become a critical parameter in their design.^{4,6} For example, to shorten the response time of a microfluidic valve, Beebe *et al.*⁶ used an array of hydrogel-coated cylinders instead of a single large diameter hydrogel-coated cylinder in the channel to take advantage of the shorter diffusion time. Ionic gels, which have great potential in the field of sensors and smart valves, need to have a short response time to ensure highly accurate results. However, ionic gels usually undergo large dynamic deformations accompanied by the migration of ions in and out of the gel as a result of a non-equilibrium ionic chemical reaction.⁶ There is therefore a need to develop theoretical models for the design and optimization of devices based on ionic gels. The exploration of the dynamic

behavior of ionic gels in response to chemical stimuli is of particular interest.

Various theories have been proposed relating to stimuli-sensitive ionic gels. Based on a simplified model coupling geometrical changes and reaction–diffusion regimes,¹⁸ Yashin and Balazs^{19,20} proposed a chemomechanical theory for self-oscillating gels driven by the Belousov–Zhabotinsky reaction. Hong *et al.*²¹ proposed another model to describe the large deformation and electrochemical behavior of polyelectrolyte gels. Their theories describe the chemomechanical behavior of the gel without using the non-equilibrium kinetics of the chemical reactions. Several workers^{22–24} have developed theoretical models to describe the response of reactive ionic gels to changes in pH and electrical fields by coupling the Donnan theories and the equilibrium theory of chemical reactions. Doi and coworkers have studied the response of ionic gels to electrical fields (chemical reactions with the assumption of fast equilibrium and non-equilibrium kinetics of diffusion in relatively large gels),²³ the dynamics of volume transition (no chemical reaction, equilibrium kinetics of diffusion),²⁵ the swelling dynamics of polymer gels under mechanical constraints, constrained thin-plate gels and cylindrical gels (no chemical reaction, equilibrium kinetics of diffusion).^{26–28} The theories proposed by these workers are independent of the non-equilibrium kinetics of the chemical reaction. Tanaka and coworkers have mainly focused on the light-scattered spectra of viscoelastic gels,²⁹ the collapse of polyacrylamide gels,⁵ the theory of the kinetics of swelling of gels (no chemical reaction, non-equilibrium kinetics of diffusion),³⁰ the phase transition of non-ionic gels,³¹ the swelling of ionic gels (chemical reaction with the assumption of fast equilibrium),²⁴ the critical kinetics of gels (no chemical reaction, non-equilibrium kinetics of diffusion),³² pattern formation in three-dimensional gels,³³ phase synchronization in self-oscillating gels (experimental study)³⁴ and thermosensitive gels used in a controlled drug-release microchip (experimental study).³⁵ These proposed theories are also independent of the non-equilibrium kinetics

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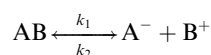
of the chemical reaction. Osada and coworkers mainly focused on electrokinetic modeling of polyelectrolyte gels,³⁶ electrically activated mechanochemical devices using ionic gels,³⁷ the reversible volume change of microparticles in an electrical field³⁸ and the worm-like motion of an ionic gel driven by an electrical field.³⁹ They do not refer to the theories of ionic gels using the non-equilibrium kinetics of chemical reactions, but mainly focus on the non-equilibrium kinetics of diffusion. There is still no non-equilibrium theory to describe the dynamic response of reactive ionic gels.

We consider here the system of a block ionic gel immersed in a dilute solution of reactive and non-reactive ions. The gel has a dynamic behavior (swelling or shrinking) as the result of a non-equilibrium chemical reaction within the gel. By coupling the theories of large deformation, the Donnan effect and the non-equilibrium kinetics of chemical reactions, a chemomechanical theory has been developed to describe the dynamic behavior of the gel. We validated the predictions from the proposed theory using existing experimental and theoretical results. As examples, we report here the oscillation deformation of an actuator changing with the period of externally applied chemical stimuli and the response time of a sensor affected by the initial state, the density of ionizable groups on the polymer and the measured concentration.

II. Kinetics OF IONIC gels

1. Chemomechanical system

When immersed in a solution containing several reactive ions, a polymer network with fixed ionizable groups begins to swell or shrink as a result of the ionic reactions between the fixed and mobile species. This results in a non-equilibrium ionic gel. We focused on a specific system, but without a loss of generality, *i.e.* a non-equilibrium process for the dissociation and association of ionizable groups



where k_1 and k_2 represent the rate constants of the forward and reverse processes, respectively (Fig. 1a and b). When the network imbibes a number of solvent molecules, the ionizable groups AB, chemically bonded on the polymer chains, dissociate into mobile ions B^+ in the solvent and conjugate bases A^- fixed on the polymer chains. During the reversible reaction, the network of polymer chains charges and discharges. For example, the increasing number of conjugate bases A^- gives rise to the fixed electrical charges of the polymer chains and consequently induces the deformation of the reactive ionic gels (forward reaction). The opposite process occurs during the backward reaction. In addition to the mobile ions B^+ and the water molecules, the solution also contains non-reactive counter ions (+) and co-ions (-). This reaction–deformation system represents the basic working mechanism of a broad range of applications, such as hydrogel-based testing devices¹⁵ and drug-delivery systems.^{12,17}

To illustrate the essential points of the method, we neglected the H^+ and OH^- ions from the dissociation of water, assuming

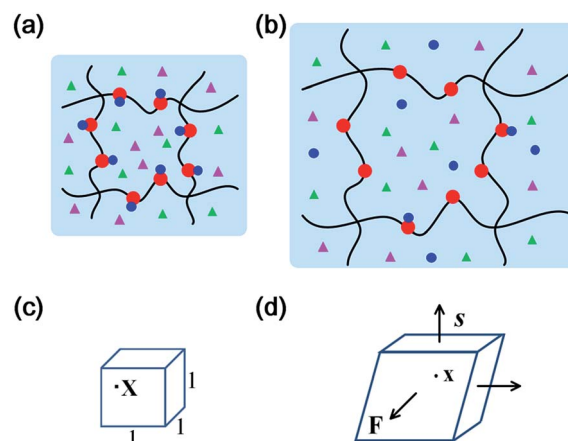


Fig. 1 An ionic polymer network immersed in a solution including several different species swells as a result of the reversible chemical reaction $AB \xrightleftharpoons[k_2]{k_1} A^- + B^+$ and a set of mechanical forces (e.g. hydrostatic pressure). Assuming that the ionizable groups AB (●) and A^- (●) are fixed on the polymer network, the species B^+ (●) freely migrate into and out of the gel; counter ions (▲) and co-ions (▲) arise from the ionization of the salt. (a) Deswelling network of polymers with fully associated ionic groups. (b) Swelling network of polymers with partly dissociated ionic groups. (c) The reference state is a unit cube of stress-free dry polymer and a mark has the initial coordinates X. (d) In the state at time t , the gel bears a stress tensor s and swells by a tensor deformation gradient F . The mark X moves to another place with coordinates $x(X, t)$ as a result of the deformation of the gel.

that their concentrations are much lower than those of the ions of interest. In addition to the polymer chains, there are six fixed and mobile species in the ionic gel system: water molecules, counter ions, co-ions, B^+ , AB and A^- . The nominal concentrations of those ions are $[C^0, C^{(+)}, C^{(-)}, C^{B^+}, C^{AB}, C^{A^-}]$ or $[C^0, C^1, C^2, C^3, C^4, C^5]$. The true concentrations are expressed as $[c^0, c^{(+)}, c^{(-)}, c^{B^+}, c^{AB}, c^{A^-}]$ or $[c^0, c^1, c^2, c^3, c^4, c^5]$ and are related to the nominal concentration by $c^\alpha = C^\alpha / \det F$, where F is defined as the deformation gradient of the gel. We used the Lagrange coordinate system in the reference configuration (Fig. 1c) and the Euler coordinate system in the current configuration (Fig. 1d). In the current state, the gel bears a stress tensor s with components s_{IK} and swells by a tensor of deformation gradient F with components F_{IK} . The function $x(X, t)$ describes the deformation field of the gel network: a material mark with the coordinate X in the reference state moves to another place with the coordinate x in the current state at time t . Consequently, F_{IK} equals $\partial x_I(X, t) / \partial X_K$.

2. Reaction kinetics

In the gel, the change in the fixed species A^- only depends on the progress of the chemical reaction. Therefore the increased number of A^- per unit volume in the current state, produced by the forward reaction during the period dt , is $k_1 c^{AB} dt$. The amount consumed by the reverse reaction is $k_2 c^{A^-} c^{B^+} dt$. Therefore the integrated change of A^- (dC^{A^-}) for the total gel volume ($\det F$) is equal to $(k_1 c^{AB} dt - k_2 c^{A^-} c^{B^+} dt) \det F$. Recalling the relationship between the true concentration and the nominal

concentration, the kinetics of the chemical reaction in the gel is given by

$$\frac{dC^{A^-}}{d\tau} = C^{AB} - \frac{k_2}{k_1} \frac{C^{A^-} C^{B^+}}{\det \mathbf{F}} \quad (1)$$

where $\tau = t/k_1^{-1}$ is the dimensionless time when adopting a time-scale of chemical reaction $\tau_R = k_1^{-1}$.

3. Thermodynamics

For the sake of reasonable simplicity, the thermodynamic analysis used a block gel with a relatively small size. As the time-scale of diffusion (τ_D) depends on the size of the gel ($\tau_D \sim L^2/D$, where L is the size of the gel and D is the diffusion coefficient),²¹ the time-scale of diffusion may be much smaller than that of the reaction in a sufficiently small gel ($\tau_D/\tau_R \ll 1$) – that is, the diffusion of the mobile species reaches equilibrium instantaneously during the chemical reaction. The dynamic behavior of the reactive ionic gels should be reaction-controlled. By neglecting the viscosity, we assumed that there is always a mechanical equilibrium in the system. Gels with a small size may be invisible, but they have been used in microchips and in microfluidic valves.^{6,35}

At a constant temperature, the ionic gel, reservoir and the mechanical force constitute a closed thermodynamic system. The gel exchanges mobile species with the external solution in the reservoir. μ^α is the electrochemical potential of the mobile species α in the reservoir – that is, the increase in the free energy of the reservoir when the reservoir gains one molecule of species α . $\delta \bar{C}^\alpha$ represents the change in the number of mobile species in the reservoir during ion exchange between the gel and the reservoir. Thermodynamics dictates that the free energy of the system should never increase:

$$\delta W + \sum_{\alpha=0}^3 \mu^\alpha \delta \bar{C}^\alpha - s_{\text{IK}} \delta F_{\text{IK}} \leq 0 \quad (2)$$

This inequality and equality hold when the system is not in, or is in, thermodynamic equilibrium, respectively. On the left-hand side, the free energy change of the system is the sum of the free energy change of the gel, the free energy change in the external solution and the potential energy change of the mechanical forces. δ represents the change of a variable over a short time period.

4. Governing equations

Water molecules, counter ions and co-ions do not participate in the chemical reactions in either the gel or the external solution. The changes in these species in the gel are entirely induced by the migration of the related molecules from the reservoir, namely $\delta C^0 = -\delta \bar{C}^0$, $\delta C^{(+)} = -\delta \bar{C}^{(+)}$ and $\delta C^{(-)} = -\delta \bar{C}^{(-)}$. However, both chemical reactions and migration contribute to the change in B^+ in the gel, *i.e.* $\delta C^{B^+} = \delta \xi - \delta \bar{C}^{B^+}$, where $\delta \xi$ is the nominal extent of the chemical reaction. The fixed species AB and A^- mutually transform from each other and cannot be produced by other mobile species, so $\delta C^{AB} = -\delta \xi$ and $\delta C^{A^-} = \delta \xi$. The total number of fixed species should be constant, *i.e.*

$C^{AB} + C^{A^-} = f/\Omega$, where f is the total number of fixed reactive species on a monomer and Ω is the approximate volume per monomer or water molecule: the densities of the ionizable group. We assumed that electroneutrality prevails both in the gel ($C^{(+)} + C^{B^+} = C^{A^-} + C^{(-)}$) and in the external solution ($\bar{c}^{(+)} + \bar{c}^{B^+} = \bar{c}^{(-)}$), where \bar{c}^α is the true concentration of species α in the external solution. For a large swelling gel in a dilute solution, the individual polymers and solvent molecules are considered to be incompressible and the total volume of ions in the gel is negligible. Consequently, when a dry gel network of unit volume imbibes a number of solvent molecules C^0 and becomes a swelling gel with a deformation gradient \mathbf{F} , the condition of volume incompressibility satisfies the relation $1 + \Omega C^0 = \det \mathbf{F}$. Considering these conditions of species conservation, ion electroneutrality and volume incompressibility, the thermodynamic inequality (2) gives the mechanical equilibrium (ESI Part 1†)

$$s_{\text{IK}} = \frac{\partial W}{\partial F_{\text{IK}}} - \Pi_1 H_{\text{IK}} \det \mathbf{F} \quad (3)$$

where Π_1 is the osmotic pressure and H_{IK} is defined as the transpose of the inverse of the deformation gradient $H_{\text{IK}} H_{\text{IL}} = \delta_{\text{KL}}$ and $H_{\text{IK}} H_{\text{JL}} = \delta_{\text{ij}}$.

The electrochemical potentials of the mobile species in the reservoir are given by

$$\mu^\alpha = \begin{cases} \frac{\partial W}{\partial C^\alpha} + \Pi_1 \Omega & \alpha = 0 \\ \frac{\partial W}{\partial C^\alpha} + (\Pi_2 - \Pi_3) z^\alpha & \alpha = 1, 2, 3 \end{cases} \quad (4)$$

where $\Pi_2 - \Pi_3$ is the Donnan potential resulting from the difference in the electrochemical potentials between the gel and the external solution. The dimensionless parameter z^α represents the valence of an ion α .

The thermodynamics derives the requirement for non-equilibrium chemical reactions as

$$\sum_{\alpha=3}^5 \frac{\partial W}{\partial C^\alpha} v^\alpha \delta \xi \leq 0 \quad (5)$$

where v^α is the coefficient of reactant α in the chemical reaction. According to our previous study,^{40,41} the kinetics of the chemical reaction in a reactive gel (eqn (1)) agree well with eqn (5) of the thermodynamics.

It is considered that there are few forces acting between the mobile species in a dilute solution: no Van-der-Waals nor any coulomb forces (*i.e.* an ideal solution). In an external solution containing several species, the chemical potential of the solvent is $\mu^0 = -k_B T \sum_{\alpha=1}^3 \Omega \bar{c}^\alpha$. Based on the Flory–Huggins theory,^{42,43} the free energy of the gel is taken to be a function of the deformation gradient and the concentration of all the species: $W = W(\mathbf{F}, C^0, C^{(+)}, C^{(-)}, C^{(B^-)}, C^{AB}, C^{A^+})$. Using the specific forms of free energy W based on the Flory–Huggins theory (ESI†), eqn (3) becomes

$$s_{\text{IK}} = N k_B T (F_{\text{IK}} - H_{\text{IK}}) - \Pi_1 H_{\text{IK}} \det \mathbf{F} \quad (6)$$

where the osmotic pressure Π_1 is specifically written as

$$\Pi_1 = k_B T \sum_{\alpha=1}^3 \left(\frac{C^\alpha}{\det \mathbf{F}} - \bar{c}^\alpha \right) - \frac{k_B T}{\Omega} \left[\ln \left(1 - \frac{1}{\det \mathbf{F}} \right) + \frac{1}{\det \mathbf{F}} + \frac{\chi + (\chi^{AB} \Omega C^{AB} + \chi^{A^-} \Omega C^{A^-})}{(\det \mathbf{F})^2} \right] \quad (7)$$

The first term on the right-hand results from the imbalance in the number of ions in and out of the gel; the second term comes from the entropy of mixing of the polymer-solvent and the enthalpy of mixing measured by a dimensionless parameter χ . The hydrating effect of the fixed species (AB and A^-) on the enthalpy of the mixing of the polymer-solvent is also characterized by the dimensionless coupling parameter χ_{AB} and χ_{A^-} , which describes the change in the hydrophobicity of the polymer chains affected by the group AB and A^- .

Considering the chemical potential of species α in the external solution with $\mu^\alpha = k_B T \ln(\bar{c}^\alpha/c_{ref}^\alpha)$, eqn (4) gives

$$c^\alpha/\bar{c}^\alpha = \exp[-(\Pi_2 - \Pi_3)z^\alpha/k_B T], \quad \alpha = 1, 2, 3 \quad (8)$$

These general equations are well known as the Donnan equilibrium.

For a free ionic gel with an isotropic stretch λ without consideration of the hydrating effect, *i.e.* $s_{IK} = 0$, $\chi^{AB} = \chi^A = 0$, combined with eqn (1) and (6)–(8), the kinetics of this reaction-deformation system are obtained (ESI[†]) as follows:

$$\frac{d\lambda}{d\tau} = \psi \frac{d\kappa}{d\tau} \quad (9)$$

$$\frac{d\kappa}{d\tau} = \frac{\zeta}{(1 + 1/\kappa^2) + 3\psi(\kappa - 1/\kappa)/\lambda} \quad (10)$$

where $\kappa = (c^\alpha/\bar{c}^\alpha)^{1/z^\alpha}$ represents the dimensionless concentration of mobile ions in the gel and ψ and ζ are expressed as:

$$\psi = \frac{\Omega(1 - 1/\kappa^2)(\bar{c}^{(+)} + \bar{c}^{B^+})}{N\Omega(3/\lambda^4 - 1/\lambda^2) + 3[1/\lambda(\lambda^3 - 1) - 1/\lambda^4 - 2\chi/\lambda^7]},$$

and

$$\zeta = \left[\frac{f/\Omega}{(\bar{c}^{(+)} + \bar{c}^{B^+})\lambda^3} - (\kappa - 1/\kappa) \right] - \frac{k_2}{k_1}(\kappa^2 - 1)\bar{c}^{B^+}.$$

The governing eqn (9) and (10) describe the deformation of the gel and the change in ion concentration in the gel during the non-equilibrium chemical reaction.

III. Numerical results and discussion

To study the dynamic response of ionic gels, we obtained solutions of the coupling equations by using a numerical method in MATLAB. In the following numerical calculations, a representative value of the volume per molecule is $\Omega = 10^{-28} \text{ m}^3$ and the number of polymer chains per unit volume of the dry network is $N = 10^{25} \text{ m}^{-3}$.²¹ To focus on the reactive kinetics in

the ionic gels, we considered the changes in the ionizable group involved in the target chemical reaction by ignoring the disturbance of neighboring acid groups on the changes in pH, *i.e.* the value of the dissociation constant $k_1/N_A k_2$ is constant. The initial state considered is that the gel instantaneously reaches mechanical equilibrium by absorbing sufficient solvent molecules while the fixed group AB rarely dissociates during this short period, *i.e.* all the fixed groups at the initial time are in the associated state AB. The initial state assumes that the gel absorbs sufficient water before the acid groups start to dissociate. The initial stretch, $\lambda_0 = 3.39$, is calculated using the equations for a non-ionic gel ($\kappa = 1$) in the mechanical equilibrium state, namely, $d\lambda/d\tau = d\kappa/d\tau = 0$.

We first validated the theoretical model by comparing the steady solutions of a previously reported pH-sensitive gel (a familiar ionic gel: A^- are carboxylic acids groups, B^+ is H^+)²² with the long time-limited solutions of our model (approximating to a steady-state). The solutions of our theoretical model at longer dimensionless times agreed well with the steady-state solutions²² (Fig. 2a and b). We then compared the swelling ratio of our theoretical predictions at longer dimensionless times ($\tau = 100$) with previously reported⁴⁴ steady-state experimental results with different concentrations of B^+ (\bar{c}^{B^+}/N_A). Here A^- is the methacrylic acid-co-acrylic acid group and B^+ is H^+ . The solutions of our theoretical model at longer dimensionless times agreed well with the previous experimental results⁴² (Fig. 2c).

In the next investigation, we focused only on the continuous deformation of the ionic gels rather than discontinuous transition. Fig. 3 shows the free swelling of an ionic gel without a loss of generality. When this gel is immersed into a solution with a constant concentration of B^+ and salt (*i.e.* $\bar{c}^{B^+}/N_A = 10^{-5} \text{ M}$, $\bar{c}^{(+)} / N_A = 10^{-3} \text{ M}$), the stretching of the gel λ varies with time as a result of the dissociation of the fixed groups (Fig. 3a), which is affected by the dissociation constants $k_1/N_A k_2$. The swelling of the gel behaves differently for different dissociation constants and reaches various equilibria after sufficient time periods. These results indicate that the chemical reaction induces the redistribution of the ionic species and the solvent molecules to reach another mechanical and electrochemical equilibrium. With increasing dissociation constants, the final stretch of the gel is larger while the response time, defined as the period required to reach the equilibrium state from the initial state, becomes longer. The reason for this is that a larger dissociation constant $k_1/N_A k_2$ means more dissociated ions at the equilibrium state of the chemical reaction, *i.e.* the network has more fixed charges A^- . Because the fixed charges must be neutralized by the counter ions, the mobile ions are more concentrated in the gel than in the external solution. The imbalance of ion concentration in and out of the gel considerably affects the osmotic pressure and therefore more solvent molecules tend to enter the gel, resulting in a larger swelling of the gel.

As a result of the longer time between the initial state and the equilibrium state with increasing dissociation constants, it takes more time to reach electrochemical and mechanical equilibrium. Fig. 3b shows a series of stretches λ of an ionic gel at different times as a function of the salt concentration in the

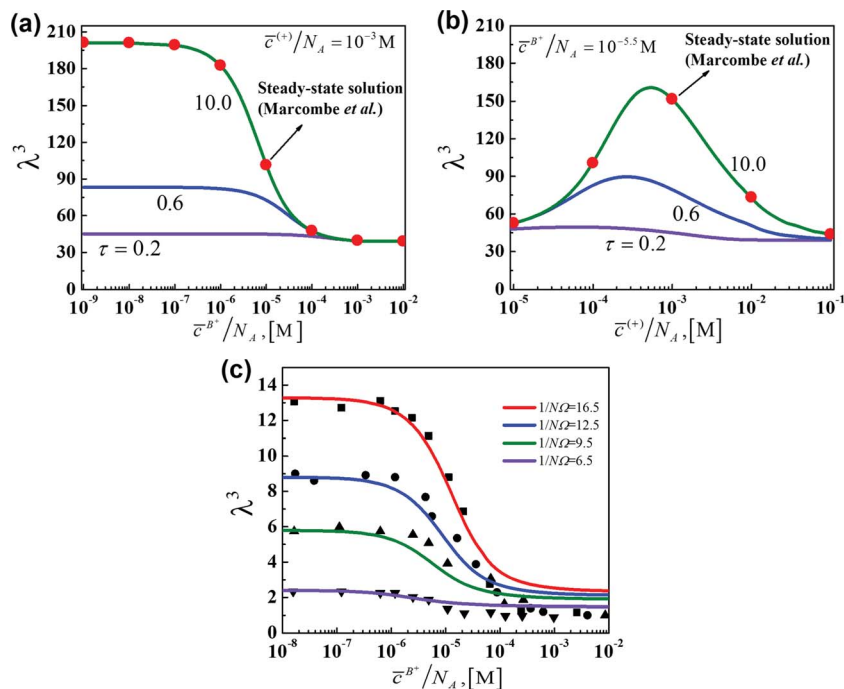


Fig. 2 The swelling ratio of a pH-sensitive gel changes (a) as a function of the concentration of B^+ (\bar{c}^{B^+}/N_A) and (b) as a function of salt concentration ($\bar{c}^{(+)} / N_A$) at different dimensionless time points. The red dots are the steady solution from Marcombe *et al.*²² The molar fraction of the ionizable group $f = 0.05$ and the dissociation constant $k_1/N_A k_2 = 10^{-4.3}$. (c) Comparison between the swelling ratio of our theoretical predictions at a longer dimensionless time ($\tau = 100$) and the experimental results at steady-state with different concentration of B^+ (\bar{c}^{B^+} / N_A). The scattered dots are experimental data from Eichenbaum *et al.*⁴⁴ and the solid lines are the simulated results from our theoretical model. Material parameters are given in ref. 30 and 31: $\bar{c}^{(+)} / N_A = 0.03 \text{ M}$, $\chi = 0.45 + 0.489/\lambda^3$, $k_1/N_A k_2 = 10^{-4.7}$, $f = 0.35$.

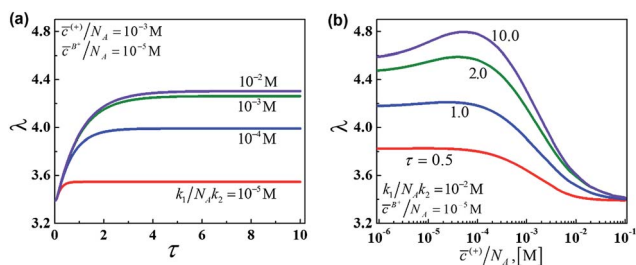


Fig. 3 Free swelling of a non-equilibrium ionic gel. The stretch λ of the ionic gel changes (a) as a function of dimensionless time with different dissociation constants ($k_1/N_A k_2$) and (b) as a function of salt concentration ($\bar{c}^{(+)} / N_A$) at different dimensionless time points.

external solution (\bar{c}_+/N_A) at a fixed concentration of B^+ and a fixed dissociation constant. With increasing dimensionless time, the stretch of the gel increases and tends to reach a steady-state at a longer dimensionless time. The dynamic behavior of the gel varies significantly depending on the salt concentration. For instance, the gel rarely deforms when the salt concentration is high ($\bar{c}^{(+)} / N_A = 10^{-1} \text{ M}$). This may be attributed to the fact that the number of counter ions in the gel is almost the same as that out of the gel, no matter how far the chemical reaction progresses. Therefore the osmotic pressure contributed by the counter ions is negligible and the gel does not swell. At lower salt concentrations the stretch of the gel significantly increases with increasing salt concentration. This is because the Donnan

equilibrium, $c^{(+)} / \bar{c}^{(+)} = c^{B^+} / \bar{c}^{B^+}$, requires that the two kinds of ions in and out of the gel are proportionally distributed. When the salt concentration is much lower ($\bar{c}^{(+)} / N_A = 10^{-6} \text{ M}$), then $\bar{c}^{(+)} < \bar{c}^{B^+}$ in the external solution and $c^{B^+} > c^{(+)}$ in the gel. The ionizable groups AB tend to a fully associated limit, resulting in a nearly neutral gel with a smaller stretch. As $\bar{c}^{(+)} / N_A$ increases, more counter ions move into the gel, resulting in the increase in gel stretch.

An ionic gel may transform chemical energy to mechanical energy through periodic volume deformation when experiencing continuous changes in the chemical environment in the external solution. For example, the gel shows an oscillating deformation with the response curves assembling separately as rectangular and saw-tooth waves. Those two characteristic response curves are at different amplitudes when the concentration of B^+ in the external solution changes rhythmically with two different periods (*i.e.* $T = 5, 25$) (Fig. 4a and b). We further assessed the influence of the period of the external stimuli on the amplitude of the deformation oscillation (Fig. 4c), which decreases rapidly with increasing frequency of external stimuli in a certain range (*i.e.* $2^{-3} < 1/T < 2^3$), but is almost unchanged when the frequency is sufficiently high or low. The reason for this phenomenon is that there is enough time for the reaction in the gel to reach the equilibrium state when the frequency of external stimuli is very low (*i.e.* the period is sufficiently long) and the amplitude of the response remains constant as long as the swelling of the gel reaches equilibrium. In contrast, there is

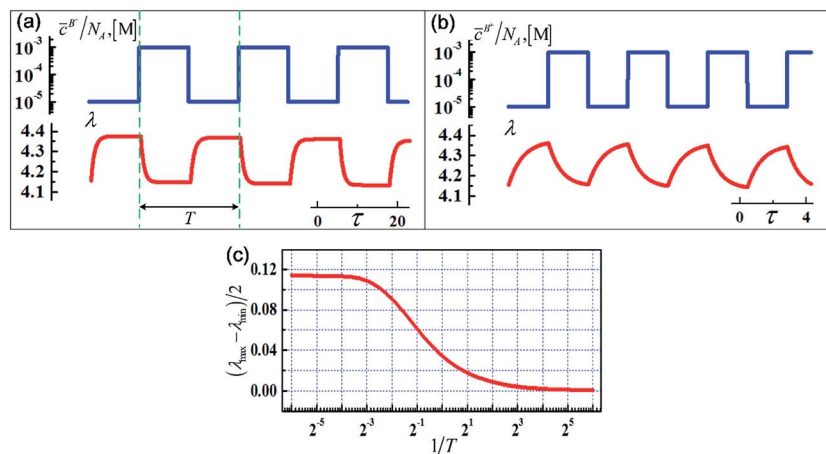


Fig. 4 Oscillating deformation of an ionic gel in response to the periodic changes in the concentration of B^+ in the external solution. Period of change (a) $T = 25$ and (b) $T = 5$. (c) The amplitude of the swelling stretch, $(\lambda_{\max} - \lambda_{\min})/2$, changes with the frequency of stimulation.

little time for the chemical reaction in the gel to evolve if the frequency of the stimuli is sufficiently high and the gel remains in a state close to the initial condition and rarely deforms.

The response time plays an important part in the accuracy of the devices based on ionic gels. To directly characterize the response behavior, the assumption is proposed that the gel is initially stored in a solution with a concentration of B^+ ($\bar{c}_0^{B^+}/N_A$) and remains in a steady-state. When a measurement is performed, the gel is transferred into a target solution with a different concentration of B^+ (\bar{c}^{B^+}/N_A) and undergoes a dynamic reaction and deformation. We consider here the reactive ionic gels with densities of an ionizable group f that can be designed. The response time τ_{eq} is defined as the period in which a gel undergoes a process to achieve 99.99% of the equilibrium deformation in response to external changes. Fig. 5 shows the response time of a gel as a function of the target concentration (\bar{c}^{B^+}/N_A) with different densities of ionizable groups ($f = 0.01, 0.02$) and different initial concentrations of B^+ ($\bar{c}_0^{B^+}/N_A = 10^{-7}, 10^{-4}$ M). For the three situations, the response time becomes longer when the target concentration is lower. This is because slower reactions in a solution with a lower concentration result in a longer response time. For each

situation shown, the blue line ($\bar{c}_0^{B^+}/N_A = 10^{-7}$ M) shows a shorter response time around the initial concentrations of B^+ ($\bar{c}^{B^+}/N_A = 10^{-7}$ M). This is because the chemical reaction is close to equilibrium ($\tau_{eq} \sim 0$) around the initial concentrations of B^+ . For the same reason, the red and green lines ($\bar{c}_0^{B^+}/N_A = 10^{-4}$ M) also show shorter response times around the initial concentration of B^+ ($\bar{c}^{B^+}/N_A = 10^{-4}$ M). The red and green lines ($f = 0.01$) represent shorter response times compared with the blue line ($f = 0.02$). The decreased response time with a smaller density of ionizable group f is related to the fact that there is a smaller number of ionizable groups available for reaction. These response characteristics of ionic gels may contribute to the design of devices for specific applications.

IV. Conclusion

A chemomechanical theory has been proposed to describe the dynamic behavior of ionic gels under non-equilibrium processes. We found that the dynamic behavior of an ionic gel depends not only on the dissociation constant of the ionizable groups on the polymer chains, but also on the concentration of the reactive and non-reactive ions in the external solution. When the ionic gel undergoes alternating stimuli from reactive ions in the external solution, the corresponding behavior is significantly affected by the frequency of the stimulus. The response time of an ionic gel for different measured concentrations of reactive ions is correlated with the initial state and the density of the ionizable groups on the polymer chains.

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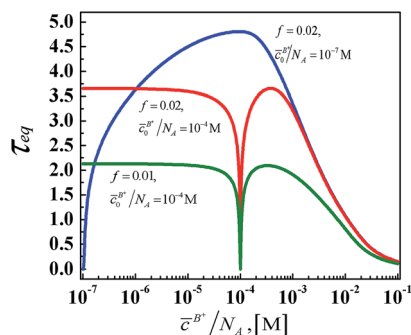


Fig. 5 Response time τ_{eq} as a function of the measuring concentration of B^+ and $\bar{c}^{(+)} / N_A$ with different initial concentrations of B^+ and $\bar{c}_0^{B^+} / N_A$ and different densities of the ionizable groups f .

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References

- 1 I. C. Chen, O. Kuksenok, V. V. Yashin, A. C. Balazs and K. J. Van Vliet, *Adv. Funct. Mater.*, 2012, **22**, 2535.
- 2 O. Kuksenok, V. V. Yashin and A. C. Balazs, *Soft Matter*, 2007, **3**, 1138.
- 3 K. Yamaki, I. Harada, M. Goto, C. Cho and T. Akaike, *Biomaterials*, 2009, **30**, 1421.
- 4 L. Dong, A. K. Agarwal, D. J. Beebe and H. Jiang, *Nature*, 2006, **442**, 551.
- 5 T. Tanaka, *Phys. Rev. Lett.*, 1978, **40**, 820.
- 6 D. J. Beebe, J. S. Moore, J. M. Bauer, Q. Yu, R. H. Liu, C. Devadoss and B. Jo, *Nature*, 2000, **404**, 588.
- 7 A. Suzuki and T. Tanaka, *Nature*, 1990, **346**, 345.
- 8 K. Okeyoshi and R. Yoshida, *Soft Matter*, 2009, **5**, 4118.
- 9 M. P. Lutolf, *Nature*, 2012, **482**, 477.
- 10 Y. Osada, H. Okuzaki and H. Hori, *Nature*, 1992, **355**, 242.
- 11 M. Lee, J. R. Williams, S. Zhang, C. D. Frisbie and D. Goldhaber-Gordon, *Phys. Rev. Lett.*, 2011, **107**, 256601.
- 12 X. Zhao, J. Kim, C. A. Cezar, N. Huebsch, K. Lee, K. Bouhadir and D. J. Mooney, *Proc. Natl. Acad. Sci. U. S. A.*, 2011, **108**, 67.
- 13 M. C. Jarvis, *Plant, Cell Environ.*, 1984, **7**, 153.
- 14 B. T. Stokke, A. Mikkelsen and A. Elgsaeter, *Eur. Biophys. J.*, 1986, **13**, 203.
- 15 Y. Zhang, H. F. Ji, G. M. Brown and T. Thundat, *Anal. Chem.*, 2003, **75**, 4773.
- 16 M. Ma, L. Guo, D. G. Anderson and R. Langer, *Science*, 2013, **339**, 186.
- 17 Y. Qiu and K. Park, *Adv. Drug Delivery Rev.*, 2001, **53**, 321.
- 18 J. Boissonade, *Phys. Rev. Lett.*, 2003, **90**, 188302.
- 19 V. V. Yashin and A. C. Balazs, *Science*, 2006, **314**, 798.
- 20 V. V. Yashin and A. C. Balazs, *Macromolecules*, 2006, **39**, 2024.
- 21 W. Hong, X. Zhao and Z. Suo, *J. Mech. Phys. Solids*, 2010, **58**, 558.
- 22 R. Marcombe, S. Cai, W. Hong, X. Zhao, Y. Lapusta and Z. Suo, *Soft Matter*, 2010, **6**, 784.
- 23 M. Doi, M. Matsumoto and Y. Hirose, *Macromolecules*, 1992, **25**, 5504.
- 24 J. Ricka and T. Tanaka, *Macromolecules*, 1984, **17**, 2916.
- 25 T. Tomari and M. Doi, *Macromolecules*, 1995, **28**, 8334.
- 26 T. Yamaue and M. Doi, *Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys.*, 2004, **69**, 041402.
- 27 T. Yamaue and M. Doi, *Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys.*, 2004, **70**, 011401.
- 28 T. Yamaue and M. Doi, *J. Chem. Phys.*, 2005, **122**, 084703.
- 29 T. Tanaka, L. O. Hocker and G. B. Benedek, *J. Chem. Phys.*, 1973, **59**, 5151.
- 30 T. Tanaka and D. J. Fillmore, *J. Chem. Phys.*, 1979, **70**, 1214.
- 31 Y. Hirokawa and T. Tanaka, *J. Chem. Phys.*, 1984, **81**, 6979.
- 32 T. Tanaka, E. Sato, Y. Hirokawa and S. Hirotsu, *Phys. Rev. Lett.*, 1985, **55**, 2455.
- 33 J. Maskawa, T. Takeuchi, K. Maki, K. Tsujii and T. Tanaka, *J. Chem. Phys.*, 1999, **110**, 10993.
- 34 R. Yoshida, M. Tanaka, S. Onodera, T. Yamaguchi and E. Kokufuta, *J. Phys. Chem. A*, 2000, **104**, 7549.
- 35 R. Yoshida, K. Omata, K. Yamaura, M. Ebata, M. Tanaka and M. Takai, *Lab Chip*, 2006, **6**, 1384.
- 36 J. P. Gong, T. Nitta and Y. Osada, *J. Phys. Chem.*, 1994, **98**, 9583.
- 37 Y. Osada and M. Hasebe, *Chem. Lett.*, 1985, **9**, 1285.
- 38 R. Kishi and Y. Osada, *J. Chem. Soc.*, 1989, **85**, 655.
- 39 H. Okuzaki and Y. Osada, *J. Intell. Mater. Syst. Struct.*, 1993, **4**, 1.
- 40 P. Wang, J. Zhou, M. Li, F. Xu and T. J. Lu, *Sci. China: Technol. Sci.*, 2010, **53**, 1862.
- 41 P. F. Wang, S. B. Liu, J. X. Zhou, F. Xu and T. J. Lu, *Eur. Phys. J. E*, 2013, **36**, 108.
- 42 P. J. Flory, *Principles of polymer chemistry*, Cornell University Press, Ithaca, NY, 1953.
- 43 M. L. Huggins, *J. Phys. Chem.*, 1941, **9**, 5.
- 44 G. M. Eichenbaum, P. F. Kiser, A. V. Dobrynin, S. A. Simon and D. Needham, *Macromolecules*, 1999, **32**, 4867.