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Advances in Mechanics of Soft Materials: A Review of Large Deformation Behavior of Hydrogels

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Hydrogels possess magnificent properties which may be harnessed for novel applications. However, this is not achievable if the mechanical behaviors of hydrogels are not well understood. This paper aims to provide the reader with a bird's eye view of the mechanics of hydrogels, in particular the theories associated with deformation of hydrogels, the phenomena that are commonly observed, and recent developments in applications of hydrogels. Besides theoretical analyses and experimental observations, another feature of this paper is to provide an overview of how mechanics can be applied.

Keywords: Hydrogel; large deformation; mechanical behavior; thermodynamic theory.

1. Introduction

When a solvent comes into contact with a network of hydrophilic crosslinked polymer chains, the attraction between the two species causes solvent molecules to be entrapped within the network, thus causing a change in volume due to the imbibement of solvent molecules. The resulting swollen state is commonly known as a hydrogel. Possessing superior capabilities to imbibe solvents and swell to a large

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extent, hydrophilic polymers, or hydrogels, are an interesting class of materials which present tremendous potential as the next generation material of choice.

Being biocompatible, many applications have been developed for hydrogels in the past few decades. Early uses of hydrogels tap on its superior bio-compatibility over plastic materials [Wichterle and Lim, 1960]. Some examples include contact lenses, wound dressings and implants [Corkhill *et al.*, 1989; Kuroyanagi, 1999; Wichterle and Lim, 1960]. Consisting of sparse crosslinks in the hydrophilic polymer network, gels are able to imbibe and retain water, causing a swelling of as large as 1000 times its initial volume [Oguz, 2007].

With different monomers or constituent particles, hydrogels are able to undergo large deformation with a small change in environmental stimulus, but not limited to temperature, pH value, light, electric field, ionic strength and magnetic field [Aguilar*et al.*, 2007; Jeong and Gutowska, 2002; Li and Kong, 2007; Meng and Hu, 2010]. These environmentally sensitive gels are also known as "smart hydrogels" and are more attractive than the traditional hydrogels, whose main attraction is its superabsorbency. However, the scope of traditional hydrogel applications is often severely limited by their mechanical behavior. For example, most hydrogels do not exhibit sufficiently high stretchability. Gong' group from Hokkaido University have successfully developed the highly strong, tough, and viscous hydrogels which have a hierarchically-ordered complex structure. These types of hydrogels will provide revolutionary applications over traditional hydrogels [Gong, 2010; Gong *et al.*, 2003; Sun *et al.*, 2013]. Their recent inventions of tough hydrogels demonstrated the potential as structural materials. These physical hydrogels have a combination of mechanical properties including stiffness, strength, toughness, fatigue resistance and self-healing, along with biocompatibility. Most recently, the Suo group from Harvard University has developed a new method for the synthesis of hydrogels from polymers forming ionically and covalently crosslinked networks [Keplinger *et al.*, 2013]. These types of gels can serve as model systems to explore mechanisms of deformation and energy dissipation, and expand the scope of hydrogel applications.

Recently, there has been a shift in interests for the choice of materials used in machines. Traditionally, machines are associated with strong and hard engineering materials, such as metals and ceramics, which are very limited by the small deformation that they are able to undergo. With more research into smart hydrogels, researchers have been attracted to tap into the new realm of soft machines, which tend to mimic what we observe in nature. The potential applications involving hydrogels has grown exponentially to include areas such as biomedical systems, actuators and flow control [Calvert, 2009; Satarkar *et al.*, 2010; Tomatsu*et al.*, 2011; Ward and Georgiou, 2011].

With the fast expanding potential for more applications in a diverse array of areas, a better understanding of the mechanics of hydrogels is imperative. In recent times, many theories have been developed to describe and understand the swelling behavior of hydrogels under the influence of various environmental stimuli and

mechanical constraints. With a better understanding of the mechanics of hydrogels, it is possible to design more applications with improved performance.

In this paper, we review some of the recent works aligned with the direction of providing a better understanding of gel mechanics, including earlier multiphase theories and more recently, the monophase theories, spearheaded by the Suo Group. Following the description of these theories, the paper then proceeds to discuss some phenomena commonly observed in gels, and how mechanics is used to study these phenomena.

The paper is organized as follows. Section 2 provides some theories on the equilibrium swelling of a gel. Section 3 covers the kinetics of swelling. Section 4 looks at the efforts in developing modeling and simulation tools. Section 5 discusses the phase transition phenomenon present in gels. Section 6 investigates the intriguing phenomenon of swelling induced instabilities.

2. Large Deformation Theories of Hydrogels

Under the influence of external stimuli, a hydrogel undergoes deformation from its initial reference state to the final current state. In describing this state of deformation, the deformation gradient F_{iK}(or $\mathbf{F}$) is conventionally used. Figure 1 shows the state of deformation of a hydrogel.

It is defined as the partial derivative of the current state of the gel, x_i, with respect to the reference state X_K, i.e.,

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

In equilibrium, the change in free energy of the gel is balanced by the external work done on the gel. This thermodynamic equilibrium is usually written in the

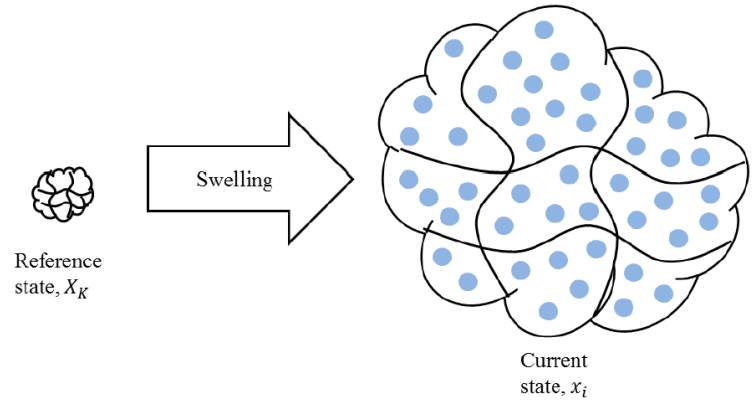


Fig. 1. A hydrogel undergoing deformation under the effects of external stimuli and changes from the reference state X_K to the current state x_i.

form

$$\int_V \delta W dV = \int_V B_i \delta x_i dV + \int_A T_i \delta x_i dA + \sum \left(\mu^r \int_V \delta C^r dV \right), \tag{2}$$

where W is the free energy of the gel; B_i is the external body force; T_i is traction; μ^r and C^r the chemical potential and concentration of the r species, which includes solvent (s) for all gels, anion ($-$) and cations ($+$) for pH sensitive gels, photochemical reactions (p) for photo-thermal gels.

By equating the change in free energy in the gel to external work done on the gel, the nominal stress s_{iK} is shown to be the partial derivative of the free energy function with respect to the deformation gradient, i.e.,

$$s_{iK} = \frac{\partial W}{\partial F_{iK}}. \tag{3}$$

The chemical potential of solvent within the gel is shown to be

$$\mu^s = \frac{\partial W}{\partial C^s}. \tag{4}$$

2.1. *Free energy functions*

The history of hydrogel deformation theory begins with pioneering works by Flory and Rehner [1943], suggesting that the Helmholtz free energy of a polymer network in an aqueous solution can be written as the additive decomposition of the free energy of elastic stretch of the polymer network and the free energy of mixing when the polymer network interacts with a solution. This decomposition has been widely used in the theories of hydrogels. According to Flory theory, the more general form of free energy of hydrogel can be described as

$$W = W_{\text{net}} + W_{\text{mix}} + \sum_{r \neq s} W_r, \tag{5}$$

where W_{net} and W_{mix} are the free energy of network stretch and free energy of mixing, respectively. These two entities are applicable to all types of hydrogels. W_r represents the free energy contributions due to factors other than solvent, which are specific to certain types of gels.

These free energies include, but are not limited to, the free energy of ionization W_{ion}, polarization W_{pol} and dissociation W_{dis}, commonly found in polyelectrolyte or pH-sensitive hydrogels; free energy of photo-chemical reactions W_{pho} in photo-thermal sensitive hydrogels; free energy of magnetization W_{mag} in ferrogels. In addition, the Landau free energy of phase transformation W_{phase} is used to represent contributions from the phase transformation process in gels. The explicit forms of each of these entities are described in the following sub-sections.

2.1.1. *Free energy of network stretch*

In all hydrogels, a deformation leads to a change in the polymer network, resulting in a change of the free energy. This contributes to the free energy of the gel in the form of the free energy of network stretch, W_{net}.

Without consideration for solvent action, the free energy of elastic stretch considers solely the stretch of the dry polymer network and is akin to the stretch of a rubber. Many forms for this free energy of rubber hyperelasticity exists [Anand, 1996; Arruda and Boyce, 1993; Boyce and Arruda, 2000; Flory and Rehner, 1943; Lopez-Pamies, 2010; Marckmann and Verron, 2006; Valanis and Landel, 1967]. The most commonly used rubber hyperelasticity model used in hydrogels is the Flory model [Flory, 1953], based on Gaussian statistics.

$$W_{\text{net}}(\mathbf{F}) = \frac{1}{2}NkT[\text{tr}(\mathbf{F}^T\mathbf{F}) - 3 - 2\ln(\det\mathbf{F})], \tag{6}$$

where N is the number of effective chains in the network and kT, product of Boltzmann constant k and temperature T, is a measure of temperature in the units of energy.

It has been noted that models lacking consideration of limited extensibility of the polymer network [Chester and Anand, 2010; Chester *et al.*, 2014] and non-Gaussian statistical models [Anand, 1996; Arruda and Boyce, 1993] have been used alternatively [Chester, 2012; Chester and Anand, 2010, 2011; Chester *et al.*, 2014] in the form

$$W_{\text{net}}(\mathbf{F}) = -NkT\left\{-\lambda_L^2\left[\left(\frac{\bar{\lambda}}{\lambda_L}\right)\beta + \ln\left(\frac{\beta}{\sinh\beta}\right) - \left(\frac{1}{\lambda_L}\right)\beta_0 - \ln\left(\frac{\beta_0}{\sinh\beta_0}\right)\right] + \left(\frac{\lambda_L}{3}\beta_0\right)\ln(\det\mathbf{F})\right\}, \tag{7}$$

where $\bar{\lambda} = \sqrt{\text{tr}(\mathbf{F}^T\mathbf{F})/3}$, λ_L is the network locking stretch parameter, $\beta = L^{-1}(\bar{\lambda}/\lambda_L)$, $\beta_0 = L^{-1}(1/\lambda_L)$, L^{-1} is the inverse of the Langevin function $L(x) = \coth x - x^{-1}$.

2.1.2. *Free energy of mixing*

As a hydrogel deforms, the volumetric change is due to the absorption or desorption of solvent molecules. The interaction between the polymer network and solvent contributes to the free energy of the system in the form of free energy of mixing.

The free energy of mixing is most commonly associated with the Flory–Huggins model [Flory, 1942; Huggins, 1941], given by the form

$$W_m(C^s) = -\frac{kT}{\nu}\left[\nu^s C^s \ln\left(\frac{1+\nu^s C^s}{\nu^s C^s}\right) + \frac{\chi\nu^s C^s}{1+\nu^s C^s}\right], \tag{8}$$

where C^s is the concentration of solvent molecules in the reference state, ν^s is the volume per small molecule and χ is the Flory interaction parameter, measuring the extent of mixing between solvent and polymer network.

In the isothermal analysis of gels, the Flory interaction parameter is usually taken to be a constant in the range of $0 < \chi < 1.2$. In temperature sensitive hydrogels, the interaction parameter is dependent on temperature and polymer concentration, originally given in the form [Huggins, 1964]

$$\chi(\phi, T) = \chi_h(\phi) + \chi_s(\phi, T), \tag{9}$$

representing the enthalpic and entropic contributions, respectively. Various experimental fittings have been performed for the dependence of χ on temperature and concentration [Afroze *et al.*, 2000; Caykara *et al.*, 2006; Erman and Flory, 1986; Hassan and Durning, 1999; Kojima *et al.*, 2013; Oliveira *et al.*, 2004; Shimizu *et al.*, 2003; Shirota *et al.*, 1998] and adopted in thermodynamic theories for temperature sensitive hydrogel models [Birgersson *et al.*, 2008; Cai and Suo, 2011; Hino and Prausnitz, 1998; Hu *et al.*, 2013a; Li *et al.*, 2005b].

2.1.3. *Free energy of ionization*

For polyeletrolyte gels, the charges in the ions give rise to ionic interactions, which include ionization and polarization. The ionization process contributes to a change in the free energy [Brannon-Peppas and Peppas, 1991; Hong *et al.*, 2010; Marcombe *et al.*, 2010; Ricka and Tanaka, 1984; Yan *et al.*, 2014].

The free energy of ionization is assumed to be entirely due to the entropy of mixing results from low concentration of ions and is given as the sum of all species r of mobile ions except the solvent,

$$W_{\text{ion}} = kT \sum_{r \neq s} C^r \left(\ln \frac{C^r}{\nu^s C^s c_0^r} - 1 \right), \tag{10}$$

where C^r is the nominal concentration of species r and c_0^r the reference concentration of species r in the solution.

2.1.4. *Free energy of polarization*

Due to uneven distribution of charges within the gel, the free energy is altered by the contribution of the free energy of polarization [Hong*et al.*, 2010; Yan *et al.*, 2014], given by the expression

$$W_{\text{pol}} = \frac{1}{2\varepsilon} \frac{F_{iK} F_{iL}}{\det \mathbf{F}} \tilde{D}_K \tilde{D}_L, \tag{11}$$

where ε is the permittivity of the gel and $\tilde{D}_i$ is the nominal electric displacement.

2.1.5. *Free energy of dissociation*

In solutions consisting of weak acids, there is partial dissociation of the acidic group AH into the hydrogen ions H^+ and conjugate base A^-

$$AH \leftrightarrow A^- + H^+. \tag{12}$$

This dissociation contributes to the free energy of the system [Marcombe *et al.*, 2010; Ricka and Tanaka, 1984] and is given by

$$W_{\text{dis}} = kT\left[C_{A^-}\ln\left(\frac{C^{A^-}}{C^{A^-}+C^{AH}}\right) + C^{AH}\ln\left(\frac{C^{AH}}{C^{A^-}+C^{AH}}\right)\right] + \gamma C^{A^-}, \tag{13}$$

where C^r are the nominal concentrations of the rth species of ions and γ is the increase in enthalpy when an acid dissociates.

2.1.6. *Free energy of photo-excitation*

In a photo-thermal gel, the light absorbing nanoparticles absorb light of particular frequencies f. This absorption results in a spontaneous excitation and decay of the outer electron, which may be represented by the chemical equation

$$X + \hbar f \to Y, \quad Y \to X + \text{heat}, \tag{14}$$

where X is the ground state particle, and Y the excited state and $\hbar f$ the energy possessed in a single photon of frequency f.

The free energy molecular excitation of the nanoparticles is associated with the product of number of photo-chemical reactions C^p and the affinity associated with a single photo-chemical reaction [Parson, 1978]

$$W_{\text{photo}} = C^p\left[\hbar f + kT\ln\left(\frac{C^p}{C^{g,0}}\right)\right]. \tag{15}$$

2.1.7. *Free energy of magnetization*

When a gel is infused with magnetic particles and exposed to a magnetic field, the magnetization of the particles have a contribution to the free energy of the gel [Han *et al.*, 2011]. One form of this free energy used is given by

$$W_{\text{mag}} = \frac{1}{2\mu^B}\mathbf{B}\cdot\mathbf{B}, \tag{16}$$

where μ^B is the magnetic permeability and $\mathbf{B}$ the magnetic induction. Equation (16) is a highly simplified expression of the free energy as it assumes no hysteresis and linear magnetic properties.

2.1.8. *Free energy of phase transformation*

In gels which undergo phase transformation, the Landau theory for phase transformation is sometimes used [Drozdov, 2014a, 2014b]. It assumes a free energy contribution of the form

$$W_{\text{phase}} = \frac{1}{\nu}\left[\frac{1}{2}A_1(T - T_*)\eta^2 + \frac{1}{4}A_2\eta^4 + \frac{1}{6}A_3\eta^6\right], \tag{17}$$

where A_1, A_2 and A_3 are constant coefficients, T_* the phase transition temperature and η is the nematic order parameter.

2.2. *Physical constraints for different hydrogels*

Physically, the constituents of the gel have to follow conservation laws. Some common physical constraints which have been used in the modeling of various types of gels are given in the following sections.

2.2.1. *Molecular incompressibility constraint*

During deformation, a gel changes volume by absorption and desorption of solvent molecules across the boundary. There is negligible change in the volumes of individual molecules as the stress that is present during swelling is insufficient to cause deformation at the molecular level.

Under this assumption, it is safe to assume that the volume of the gel is equal to the sum of volume of the constituent polymer and the solvent within the network. This constraint is most commonly expressed as

$$1 + \nu C^s = \det \mathbf{F}. \tag{18}$$

2.2.2. *Electroneutrality*

As a simplification in polyelectrolyte gels, it is assumed that the overall charge on the gel and in the external solution is neutral. This assumption gives rise to the following expressions

$$C^{H^+} + C^+ = C^{A^-} + C^-, \tag{19}$$

$$\bar{n}^{H^+} + \bar{n}^+ = \bar{n}^-, \tag{20}$$

where C^r are the nominal concentrations of the superscripted species and $\bar{n}^r$ the number of particles of the superscripted species in the external solution.

2.2.3. *Energy conservation*

In photothermal sensitive hydrogels, the photo-excitation of light absorbing particles is a spontaneous process. The energy absorbed from light excites an electron to the

outer shell and is immediately demoted back to its original energy level, and the energy released from this demotion is converted into heat energy.

Due to near unity conversion from light energy to thermal energy, energy conversion can be written in the form

$$[c_v^{\text{network}}\phi + c_v^s(1-\phi)]\alpha I_0 = hfC^p \det \mathbf{F}, \tag{21}$$

where the left-hand side corresponds to thermal energy and the right-hand side corresponds to light energy. c_v^r represents the volumetric heat capacity of the network and solvent molecules, α is a proportionality constant, I_0 is the intensity of the monochromatic light irradiation with frequency f, $\hbar$ is the Planck constant, and C^p the nominal concentration of photo-chemical reactions taking place.

2.3. *Imposition of physical constraints*

2.3.1. *Lagrange multiplier*

The enforcement of these physical constrains are usually carried out in two ways. First through the addition of Lagrange multipliers to the thermodynamic equilibrium equation [Baek and Pence, 2011; Baek and Srinivasa, 2004; Duda *et al.*, 2010; Hong *et al.*, 2010; Hong *et al.*, 2008b]. This method leads to nominal stress and chemical potentials being functions of the Lagrange multiplier, as seen in Eqs. (22) and (23) for the case of a neutral gel

$$s_{iK} = \frac{\partial W}{\partial F_{iK}} - \Pi H_{iK} \det \mathbf{F}, \tag{22}$$

$$\mu^s = \frac{\partial W}{\partial C^s} + \Pi \nu^s. \tag{23}$$

The Lagrange multiplier Π is an inhomogeneous field, solvable as part of initial and boundary value problems. In a neutral hydrogel, it is analogous to the osmotic pressure due to the external solvent. Li *et al.* [2012] and Cai and Suo [2012] investigated Π as an equation of state for ideal elastomeric gels.

2.3.2. *Legendre transformation*

An alternative method is through the use of a Legendre transformation of the free energy function [Ding*et al.*, 2013; Hong *et al.*, 2009a; Marcombe *et al.*, 2010; Toh *et al.*, 2014a]

$$\hat{W} = W - \sum \mu^r C^r, \tag{24}$$

where expressions for C^r are obtained using the constraint equations (18), (19) and (21).

The transformation converts the thermodynamic equilibrium equation into one which is represented by a hyperelastic solid

$$\int_V \delta \hat{W} dV = \int_V B_i \delta x_i dV + \int_A T_i \delta x_i dA. \tag{25}$$

Under this definition, the nominal stress is shown to be

$$s_{iK} = \frac{\partial \hat{W}}{\partial F_{iK}}. \tag{26}$$

The constitutive equation of gel materials may be defined using the forth order tangent modulus tensor, C_{ijkl} [Kang and Huang, 2010c].

In equilibrium, the concentration of solvent within the swollen gel is homogeneous in the absence of external mechanical constraints. However, in the presence of such constraints, the concentration becomes inhomogeneous despite being in mechanical equilibrium [Hong *et al.*, 2009a; Pritchard and Terentjev, 2013; Zhao *et al.*, 2008]. In addition, the presence of a surface causes a shift in equilibrium of the gel between the saturated state, unsaturated state and a gel in equilibrium with a vapor of its own liquid [Baek and Pence, 2011].

A widely observed phenomenon in gels is volume phase transition, where a small change in stimulus causes a sudden large deformation in the gel. Experimental results have shown that the phase transition process can be continuous or discontinuous at different times, depending on the constituents and environmental conditions [Suzuki, 1993]. Factors influencing this shift from continuous to discontinuous phase transition include, but are not limited to, light, temperature, applied stress and pH-value [Kondo *et al.*, 1993; Suzuki *et al.*, 1996; Suzuki and Kojima, 1994; Suzuki and Suzuki, 1995; Suzuki and Tanaka, 1990]. Various models have been proposed to study this phenomenon [Cai and Suo, 2011; Toh *et al.*, 2014a; Wang, 2007]. The Landau free energy function for phase transition has also been used to circumvent the discontinuity in phase transitions [Drozdov, 2014a, 2014b].

3. Swelling Kinetics of Hydrogels

3.1. *Multi-phase theories*

Earlier theories of gel swelling were based on considering the polymer network and solvent as two separate phases. Works by Tanaka *et al.* made use of equations derived based on Newton's second law with inclusion of the effects of friction, relative motion and viscosity between the phases [Peters and Candau, 1986, 1988; Tanaka and Fillmore, 1979; Tanaka *et al.*, 1973]. Later, a two-step mechanism was proposed to generalize the swelling kinetics of gels of arbitrary shapes [Li and Tanaka, 1990].

A coupling relation between stress and gel composition was proposed by using phenomenological hydrodynamic relations, treating the gel as a two-fluid model [Calderer *et al.*, 2008; Doi, 2009; Doi and Onuki, 1992; Yamaue and Doi, 2004a; Yamaue and Doi, 2004b; Yamaue and Doi, 2005].

These theories provide a very detailed analysis of gel properties. However, they are limited by the relative difficulty in implementing simulations to aid researchers in understanding material response under more complex situations.

3.2. *Mono-phase theory of hydrogel*

The swelling of a gel using a continuum approach was pioneered by Durning and Morman [1993] to overcome the shortcomings of the hydrodynamic models proposed in the multi-phase approach, motivated by the relative complexity of multi-phase theories and also the ease of single continuum implementation. Baek and Srinivasa [2004] proposed a monophase theory for a solvent diffusing through an elastic solid.

However, monophase theories were not favored until more recently, when the Suo Group from Harvard proposed a more unified thermodynamic framework coupling diffusion and large deformation in a gel [Hong *et al.*, 2008b]. With many promising applications lying ahead for hydrogels, mono-phase theories have gained increasing popularity against multi-phase theories due to the relative ease of modeling and simulation of material behaviors. This thermodynamic framework has spurred much interests in the monophase theory, as seen from the numerous works stemming from the same framework [An *et al.*, 2010; Bouklas and Huang, 2012; Chester, 2012; Chester and Anand, 2010, 2011; Duda *et al.*, 2010; Hong *et al.*, 2010; Lucantonio *et al.*, 2013].

Whilst using the Flory–Rehner model has been widely adopted for study of gel swelling, there lies a less than unified theory for the study of gel swelling kinetics, as some theories consider the polymer network and fluid to be distinct phases for the robustness. Some theories treat the polymer-fluid interaction as a single phase by coupling the diffusion of solvent with the large deformation of the network, simplifying the development process of numerical simulation methods used to predict the response of hydrogels.

The deformation gradient is often based on a multiplicative decomposition of elastic and swelling parts [Boyce and Arruda, 2001; Chester and Anand, 2010; Duda *et al.*, 2010], written as

$$\mathbf{F} = \mathbf{F}^e\mathbf{F}^s. \tag{27}$$

However, it was noted that in the swelling of a polymeric gel over an extended time-span, the elastic part of the deformation may be taken to be an instantaneous process and for modeling of the migration of solvent molecules into the gel, it may be taken to be unity [Hong *et al.*, 2008b]. Indeed, in equilibrium studies, we are concerned with the end state deformation rather than the initial change in deformation.

3.3. *Neutral gel*

Baek and Srinivasa [2004], Hong *et al.* [2008b], Duda *et al.* [2010] and Chester and Anand [2010] have developed thermodynamic theories which couple diffusion and large deformation, paving the way for future works in the continuum mechanics studies of hydrogel swelling.

The governing equations of gel swelling are dependent on the migration of solvent molecules. The flux is given by

$$j_i = \frac{cD}{kT}\frac{\partial \mu}{\partial x_i}, \tag{28}$$

and it follows conservation laws, given by the form

$$\int_V \frac{1}{\det \mathbf{F}}\frac{\partial C}{\partial t}dV + \int_A j_i dA = 0. \tag{29}$$

Based on the coupled diffusion-deformation theory, Yoon *et al.* [2010] developed a linearized poroelastic swelling kinetic theory to characterize material properties such as the modulus, Poisson's ratio and permeability of a gel swelling within the regime of linear poroelasticity. A comparison with the nonlinear theory has shown the linear theory to be consistent within the linear portion of swelling [Bouklas and Huang, 2012].

3.4. *Temperature sensitive gel*

Birgersson *et al.* [2008] developed a model for the transient response of a temperature sensitive hydrogel by considering conservation laws for the polymer and fluid phase separately using the mixture theory. Analysis takes place in a nondimensional framework to elucidate important characteristics as well as simplify the governing equations. In addition to fluid transport, the kinetic laws of a temperature sensitive hydrogel also depends on the temperature gradient of the gel, which may be modeled using Fourier's laws of heat conduction, given in Eqs. (30) and (31)

$$q_i = -\kappa\frac{\partial T}{\partial x_i}, \tag{30}$$

$$\int_V \rho\frac{dU}{dt}dV + \int_A q_i dA = \int_V r dV. \tag{31}$$

By considering entropy imbalance, Chester and Anand [2011] extended the coupled theory for fluid permeation in elastomeric materials [Chester and Anand, 2010] to account for thermal response in temperature-sensitive hydrogels.

3.5. *Polyelectrolyte gel*

Kinetic theory of polyelectrolyte gels (pH gels) are mostly assumed to follow the Nernst–Planck equation of ion diffusion kinetics [Helfferich and Plesset, 1958]. Other than kinetic laws based on diffusion, the distribution of ions within the gel is also dependent on ionic interactions, following the Nernst–Planck equation

$$j_i^r = -D^r\left[\frac{\partial C^r}{\partial x_i} + z^r C^r\left(\frac{\mathbf{F}}{RT}\right)\frac{\partial \psi}{\partial x_i}\right], \tag{32}$$

where the superscript r denote the rth species of ion, D^r is the diffusion coefficient, C^r is the concentration, z^r is the valency number, $\mathbf{F}$ is the Faraday

constant, R is the gas constant, T is the temperature, and ψ is the electric potential.

4. Numerical Simulation of Hydrogels

To predict the behavior of hydrogels, numerical simulation is commonly used as it allows for studying gels of complex geometries which are often too complicated for any analytical solutions.

Common simulation tools used in the study of hydrogel behaviors include finite element method, meshless methods and molecular dynamics simulations.

4.1. *Finite element method*

With the development of monophase theories, finite element simulation of hydrogel swelling has been expedited, in particular with the use of finite element software ABAQUS for its versatility in defining material models through user-defined subroutines. Besides ABAQUS, there has also been finite element simulations performed using COMSOL Multiphysics and on other platforms. Nevertheless, it should be noted that simulation using ABAQUS is one of the most popular methods as the solver is capable of solving highly nonlinear cases. Common subroutines used for equilibrium swelling include UHYPER [Ding *et al.*, 2013; Hong *et al.*, 2009a; Marcombe *et al.*, 2010; Toh *et al.*, 2014a], which models the equilibrium swelling of a gel as a hyperelastic material through a Legendre transformation; and UMAT [Ding *et al.*, Under review; Kang and Huang, 2010c], which requires the tangent modulus tensor as input. Advantages of UHYPER over UMAT include easy implementation and less computational time. On the other hand, UMAT provides a more robust simulation, enabling the use of anisotropic initial conditions, as UHYPER requires isotropic initial conditions.

The finite element models for swelling kinetics of gels include the use of one or more subroutines used concurrently. Zhang *et al.* [2009] and Chester *et al.* [2012; 2011; 2014] have made substantial contributions in the area of developing user-defined elements (UEL subroutine) for the simulation of neutral, viscoelastic and temperature sensitive hydrogels. It should be noted that the development of UEL subroutines is a tedious process, as it involves much work on the discretization of elements. A discretization has to be performed for every element type that is required for simulation. Less rigorous methods have also been developed for the same purpose by utilizing the coupled temperature-displacement elements already present in the ABAQUS library, thus eliminating the need for re-formulation of elements [Duan *et al.*, 2013; Toh *et al.*, 2013; Toh *et al.*, 2014b].

Owing to the powerful multiphysics coupling mechanism present, COMSOL Multiphysics is a popular software of choice for simulation of heavily coupled physical material models. The software has been used to simulate transient swelling kinetics of polymeric gels [Lucantonio *et al.*, 2013], viscoelastic polymer gels [Li *et al.*,

2013b; Wang and Hong, 2012], temperature sensitive gels [Birgersson *et al.*, 2008] and ferrogels [Han *et al.*, 2011].

Wallmersperger *et al.* [2011a, 2011b] developed a chemo-electro-mechanical finite element model to solve for the equilibrium swelling of pH-sensitive gels, taking into account effects of various ions and their interactions. Liu *et al.* [2015] developed a finite element algorithm based on the multiplicative decomposition of deformation gradient to simulate the inhomogeneous swelling of neutral hydrogels in equilibrium state.

Dolbow *et al.* studied the kinetics of hydrogels based on the motion of the sharp interface between difference phases of the gel using the extended FEM (XFEM) method [Dolbow *et al.*, 2004, 2005; Ji *et al.*, 2006].

4.2. *Meshless methods*

Apart from the finite element method, meshless methods are also very popular for simulation of hydrogels. However, for meshless methods, there is a wide spectrum of approaches which has been used in the modeling of gel materials. These include the improved complex variable element-free Galerkin (ICVEFG) method on neutral hydrogels [Li *et al.*, 2014], strong-form meshless random differential quadrature (RDQ) method [Li and Mulay, 2011], and finite cloud method on pH-sensitive gels [De and Aluru, 2004; De *et al.*, 2002] and Hermite–Cloud method on electric-sensitive hydrogels [Chen *et al.*, 2005; Lam *et al.*, 2006; Li, 2009; Li *et al.*, 2003, 2006, 2007a; Li *et al.*, 2007c; Luo *et al.*, 2007]; pH-sensitive hydrogels [Li *et al.*, 2005a; Li and Yew, 2009; Li *et al.*, 2004; Li *et al.*, 2005c; Ng *et al.*, 2010]; electric-pH sensitive hydrogels [Li *et al.*, 2007b; Luo *et al.*, 2008]; and ionic strength sensitive hydrogels [Lai and Li, 2010, 2011; Li and Lai, 2011].

4.3. *Molecular dynamics simulations*

In simulations of smaller length scales, variations of molecular dynamics (MD) has also been used, such as a combined discontinuous molecular dynamics and Monte Carlo technique [Kenkare *et al.*, 2000], as well as coarse grained molecular dynamics [Quesada–Perez *et al.*, 2012]. In coarse grained dynamics model, Quesada–Perez *et al.* adopted coarse grained molecular dynamics to simulate the steady state swelling behavior of gels due to temperature and pH changes. The truncated Leonard–Jones potential was used for interaction between particles and a hydrophobic interaction potential. Jaramillo–Botero *et al.* [2010] investigated the thermodynamic and mechanical properties of polymer-based hydrogel networks by using atomistic-level molecular dynamics. The study provided insights into elastic response, cohesive energies, viscosities, and stress–strain relationships for relevant single and double network hydrogel compositions from atomistic level. The works can be used for steering experimental efforts toward systematic optimization of the bio-mimetic response of polymer-based scaffolds in tissue engineering. Sliozberg

et al. [2014] used computational coarse-grained model to design complex polymer networks and gels, in which the enhanced and tunable mechanical properties are obtained. The elastic properties and deformation mechanisms of the polymers were also investigated by tensile test at various strain rates. Their studies demonstrated that the architecture of the polymer can be optimized and thus the elastic properties can be tuned for specific engineering applications.

5. Some Phenomenon Related to Gel Deformation

5.1. *Phase transition*

In the gel deformation process, it is commonly observed that across a critical loading parameter, the volume change of the gels occurs drastically. This phenomenon is known as the phase transition of a gel. Experimentally, the phase transition has been observed in hydrogels responsive to different types of environmental stimuli. The Tanaka group from MIT has performed substantial work on the phase transitions in various types of gels, which include ionic gels [Ohmine and Tanaka, 1982; Tanaka *et al.*, 1980], nonionic gels [Amiya *et al.*, 1987; Hirokawa and Tanaka, 1984], temperature sensitive gels [Hirose *et al.*, 1987; Hirotsu *et al.*, 1987] and photosensitive gels [Mamada *et al.*, 1990; Suzuki and Tanaka, 1990]. Suzuki *et al.* from the Yokohama National University of Japan explored the effects of several factors on the phase transition of gels, including uniaxial stress [Kondo *et al.*, 1993; Suzuki and Kojima, 1994], pH-value [Suzuki and Suzuki, 1995] and light [Suzuki and Tanaka, 1990]. Juodkazis *et al.* [2000] studied the effects of radiation forces on hydrogels.

Cai and Suo [2011] developed a thermodynamic theory of deformation in temperature sensitive hydrogels and studied the phase transition phenomenon of temperature sensitive hydrogels. In addition, the model was applied to study the phase coexistence between gels of different phases. Ding *et al.* [2013] reported that in temperature sensitive hydrogels, other than the critical temperature, there is also a critical chemical potential which causes phase transition. Toh *et al.* [2014a] developed a thermodynamic theory for photo-thermal sensitive hydrogels and studied the effects of light intensity on the phase transition.

5.2. *Instabilities*

Mechanical instabilities, such as wrinkling, creasing, buckling and bifurcation are commonly observed phenomenon in hydrogels [Barros*et al.*, 2012; Douezan *et al.*, 2011; DuPont Jr. *et al.*, 2010; Guvendiren *et al.*, 2009; Ji and Ding, 2002; Kim *et al.*, 2010; Klein *et al.*, 2007; Lee *et al.*, 2014; Liang and Mahadevan, 2011; Matsuo and Tanaka, 1992; Peixinho and Mukhopadhyay, 2013; Savin *et al.*, 2011; Sultan and Boudaoud, 2008; Tanaka *et al.*, 1992; Tanaka *et al.*, 1987; Wu *et al.*, 2014; Zhu *et al.*, 2012]. These mechanical instabilities, initially deemed to be undesirable, have recently become the subject of interest, with the instabilities exploited for useful applications, such as tunable adhesion, micro-patterning, particle sorting,

microfluidics, microfabrication and actuation [Chen and Yang, 2012; Chen and Yin, 2010; Hu *et al.*, 1998; Kwon *et al.*, 2010; Yang *et al.*, 2010].

These exciting potential applications have spurred many theoretical analyses of the instability, with analyses in several broad areas, including:

5.2.1. *Bilayer structures*

The most commonly studied model for swelling induced instabilities in soft materials is the bilayer structure, where a thin layer of gel film is bounded to a substrate (Fig. 2), such as an elastic substrate [Cai *et al.*, 2011; Huang and Suo, 2002a, 2002b; Huang *et al.*, 2004; Jia and Ben Amar, 2013; Kang and Huang, 2010b; Liu *et al.*, 2010; Liu *et al.*, 2011] or a gel substrate of different material properties [Wu *et al.*, 2013].

The buckling of bilayer structures present many interesting buckling patterns, such as the herringbone, labyrinth patterns, peanut, lamellar and hexagonal structures [Cai *et al.*, 2011; Guvendiren *et al.*, 2009].

For soft-on-hard bilayer structures, creasing instability takes precedence over wrinkling. On the other hand, hard-on-soft bilayer structures first grow wrinkles before transitioning into creases [Lee *et al.*, 2008; Wu *et al.*, 2013].

In addition to flat bilayer structures shown in Fig. 2, there have also been many studies on spherical bilayer structures, or core-shell structures. Spherical core-shell soft structures exhibit various morphologies, such as the buckyball, deformed polygons and labyrinth patterns [Fogle *et al.*, 2013; Komura *et al.*, 2005; Li *et al.*, 2011b; Yin *et al.*, 2008]. The study of such morphologies provides an insight on the growth of biological systems, such as tumors.

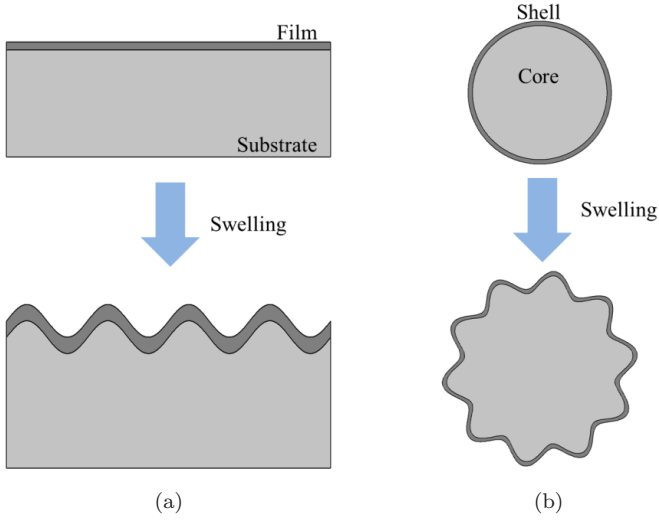


Fig. 2. Surface wrinkling of a bilayer structure. (a) Film attached to a substrate and (b) a core-shell structure.

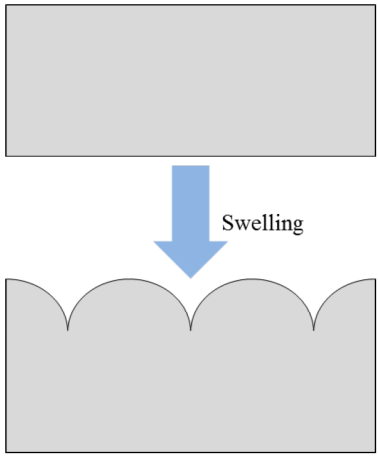


Fig. 3. Surface creasing of a thick hydrogel layer.

5.2.2. *Surface instabilities of thick gel layers*

When fixed to a rigid substrate, a thick gel layer with uniform [Ben Amar and Ciarletta, 2010; Hong *et al.*, 2009b; Trujillo *et al.*, 2008; Weiss *et al.*, 2013; Xiao *et al.*, 2012] and nonuniform crosslink densities [Guvendiren *et al.*, 2009; Wu *et al.*, 2013] experience surface instabilities, as illustrated in Fig. 3.

These surface instabilities are mainly in the form of creasing as stability analysis has shown that the onset of creases on the surface requires a considerably lower critical swelling ratio [Jin *et al.*, 2011; Jin *et al.*, 2014; Wong *et al.*, 2010]. Surface tension aids to suppress short wavelength instabilities [Kang and Huang, 2010a].

During swelling, wrinkles may appear during the transient process due to compressive stresses being induced. Over the time evolution, the stress distribution changes and thus causes the wrinkles to evolve from one wavelength to another. This phenomenon has been observed repeatedly in experiments [Guvendiren *et al.*, 2010; Peixinho and Mukhopadhyay, 2013; Tanaka *et al.*, 1992; Tanaka *et al.*, 1987]. Toh *et al.* [2015] modeled and investigated the evolution of wrinkle wavelengths using finite element and linear perturbation methods.

5.2.3. *Bulk buckling of thin gel films*

Thin gels geometrically constrained at certain points buckle into periodic wrinkles during the swelling process. Figure 4 shows the wrinkling patterns of an annular gel and a gel strip. Experimentally and theoretically, it has been shown that the wavelength of the wrinkles depend on the geometry of the gel [Lee *et al.*, 2012; Li *et al.*, 2013a; Liu *et al.*, 2011; Mora and Boudaoud, 2006; Zhang *et al.*, 2014].

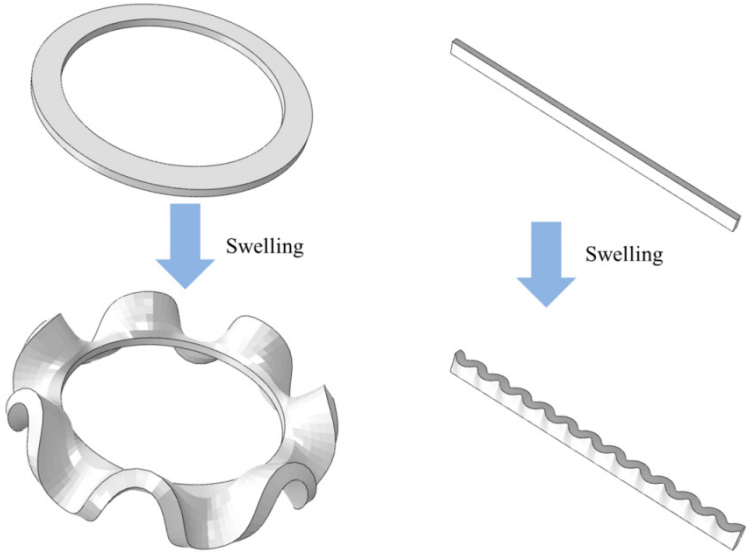


Fig. 4. Buckling into waves of different sizes of (a) gel annulus constrained on inner side and (b) gel strip constrained on 1 side.

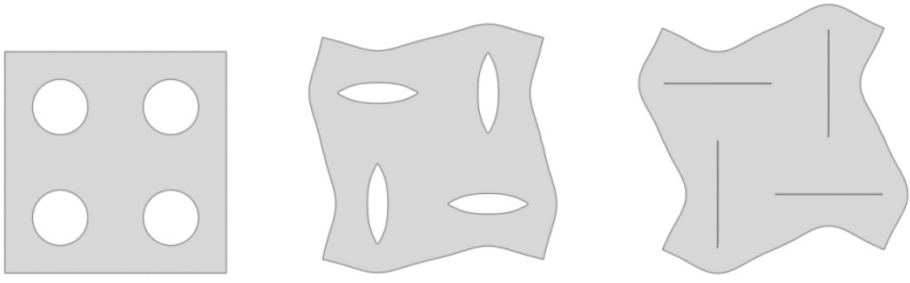
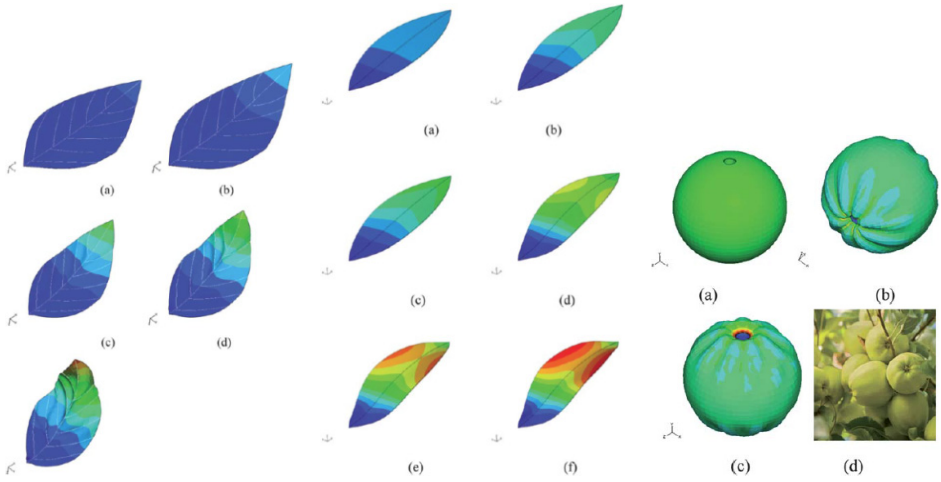


Fig. 5. (a) Gel film initially with perfect circular geometry, (b) transits into elliptical holes with mutually perpendicular orientations, and (c) the elliptical holes close up to form mutually perpendicular slits.

5.2.4. *Bifurcation of gel films with square lattice of holes*

In gel layers with periodic holes arranged in an array, the instability is not in the form of surface wrinkles. Instead, the holes bifurcate into alternating perpendicular slits (Fig. 5) [Bertoldi *et al.*, 2008; Mullin *et al.*, 2007; Okumura *et al.*, 2014].

Okumura *et al.* studied the effects of geometrical imperfections [Okumura *et al.*, 2014] and prestrain [Okumura *et al.*, 2015] on the resulting geometry. It was shown that while three buckling patterns were obtained, the diamond pattern was thermodynamically most favorable due to the lower stress level present.



(a) (b) (c)

Fig. 6. (a) The drying of a leaf, simulated by the dwelling of a hydrogel. (b) The growth of a leaf, simulated by the swelling of a hydrogel. (c) The formation of ripples in an apple, simulated by differential swelling between different layers of hydrogel [Liu *et al.*, 2010; 2013].

5.3. *Explanation of natural phenomena*

The use of soft materials to mimic natural phenomenon is getting more and more prevalent. Further, with the development of ABAQUS finite element subroutines, the instability of gels has been used to model and explain phenomena commonly observed in nature. Cao *et al.* [2012] likened the volumetric growth process to thermal stress to study wrinkle formation on skin. Amar and Goriely [2005] and Li *et al.* [2011a] modeled the growth process using an incremental deformation theory to study growth of soft tissues and mucosa, respectively.

On the other hand, Liu *et al.* [2010; 2013] made use of the volume change in hydrogels to model growth and the drying processes, which is a more realistic approach for studying the geometrical features of plants or phyllotaxis (as shown in Fig. 6). Similarly, Dervaux and Amar [2011] likened the growth of a tumor to the swelling of a hydrogel. This is achieved by modeling these items as hydrogels or soft materials, which are able to undergo volumetric expansion and shrinking, thus simulating the growth and drying processes and the associated buckling phenomena as energy minimizing mechanisms.

6. Applications for Soft Machines

In the emerging field of soft machines, hydrogels are the most viable and valuable candidate of soft materials that can provide extremely large deformation. Thus, with more research into smart hydrogels, the potential applications involving hydrogels has grown exponentially. Generally, individual standalone soft materials are not

able to provide all of the requisite functions for soft machines; rather, soft machines are mostly hybrids of soft and hard materials. However, some hydrogels do possess the properties required for stretchable electronics applications, and can deform in response to stimuli other than mechanical forces.

6.1. *Microfluidics*

Hydrogels have been shown to be able to function well as flow control devices [Baldi *et al.*, 2002; Harmon *et al.*, 2003; Johnson *et al.*, 2004; Lai *et al.*, 2007; Moore *et al.*, 2000; Satarkar *et al.*, 2009; Sugiura *et al.*, 2007; Wang *et al.*, 2005] in micro systems. Various configurations and designs have been proposed, but a common technique is making use of the contact stress between a swollen gel and a rigid structure to restrict flow movement across a channel. Figure 7 shows two types of mechanisms in which hydrogels are utilized in microfluidic devices.

Through understanding of gel mechanics, it is possible to better design such applications. Zhang *et al.* [2012] and He *et al.* [2012] modeled pH-sensitive hydrogel valves, studying the fluid-structure interaction and contact stresses within these valves.

6.2. *Self-assembled structures*

With localized application of external stimuli, it is possible to program a gel to swell and fold in a certain way, thus forming self-folding smart structures. Ryu *et al.* [2012] introduced a self-folding box using localized light absorption and Na *et al.* [2015] demonstrated a reversible self-folding crane using trilayer films.

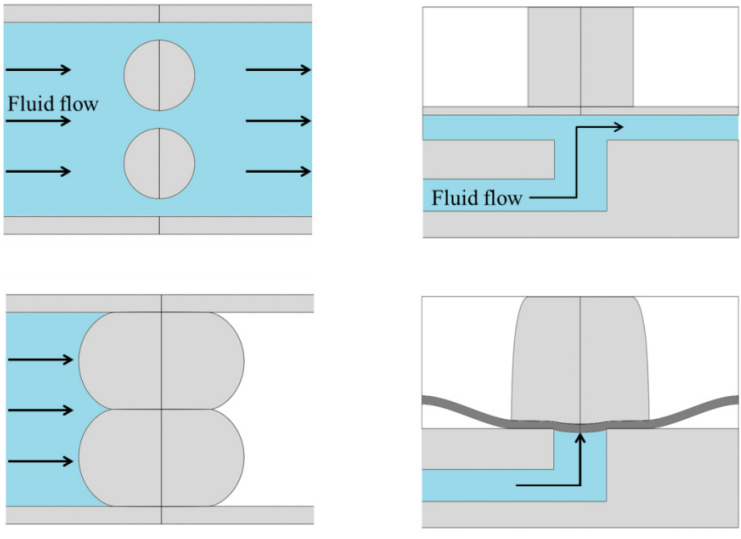


Fig. 7. The examples of hydrogel actuated microfluidic valves.

The swelling induced buckling of gels can be harnessed for a novel way to create gear systems [Yin *et al.*, 2009; Zhang *et al.*, 2010]. More recently, Hu *et al.* discovered a negative Poisson ratio phenomenon in soft materials, which holds promising applications for novel structures [Hu *et al.*, 2013b; Hu *et al.*, 2014].

6.3. *Sensors and actuators*

When bound to a substrate, a gel structure undergoes differential swelling and bends as a result. This effect is useful for actuation [Bassik *et al.*, 2010; Hoffmann *et al.*, 1999; Hong *et al.*, 2008a; Kim *et al.*, 2011; Wang *et al.*, 2013]. As compared to traditional actuators made from more conventional engineering materials, gel actuators allow for a larger extent of actuation due to the larger deformations.

Other than machines, hydrogel actuators also hold a promising future as artificial muscles due to their bio-compatibility [Bassil *et al.*, 2008; Bassil *et al.*, 2011; Mirfakhrai *et al.*, 2007].

The large deformation, coupled with environmentally responsive properties of certain types of gels, also make for very good sensors [Bashir *et al.*, 2002; Richter *et al.*, 2008; Sheppard Jr. *et al.*, 1995; van der Linden *et al.*, 2003; Zhang *et al.*, 2004].

6.4. *Tunable lens*

With the prevalence and advancement of mobile phone cameras, the trend of taking photos is slowly evolving toward phones replacing cameras. Due to their cumbersome implementation, removable hard lens are losing popularity. This compromises on the quality of photographs being taken. However, soft lens are able to solve this problem, as the degree of curvature and thickness of a gel lens can easily be altered using external stimuli, such as temperature [Zeng *et al.*, 2010] and pH-value [Zalachas *et al.*, 2012].

Due to large deformation, creases may form in the microlens. Zalachas *et al.* [2013] modeled the creasing instability that arises in such configurations.

6.5. *Drug delivery*

Making use of characteristic properties of different parts of a body, hydrogels can be customized to target specific areas for drug release [Chu, 2003; Elvira *et al.*, 2004; Giani *et al.*, 2012; Gupta *et al.*, 2002; Jeong *et al.*, 2006; Liu *et al.*, 2006; Qiu and Park, 2001; Satarkar and Hilt, 2008; Siepmann *et al.*, 1999; Uva *et al.*, 2014; Zhao *et al.*, 2010]. In the drug delivery process, it is imperative that the deformation kinetics be fully understood.

6.6. *Hydrogel ionic conductors*

Hydrogel ionic conductors make it possible to develop new stretchable electronic devices. The Harvard group has developed a class of new devices enabled by ionic conductors. In these devices, the ionic conductors are highly stretchable, and fully

transparent to light of all colors [Keplinger *et al.*, 2013]. In their study, they reported that the transparent actuator can generate large strains and also act as a transparent loudspeaker. They highlighted that in the device, the electromechanical transduction can work without any electrochemical reaction. This achievement based on ionic conductors is advantageous over the existing stretchable, transparent electronic conductors. Their findings provide possibilities of an alternative stretchable ionic conductor based on a deformable hydrogel device.

7. Potential Research Directions of the Mechanics of Hydrogels

Much work remains to be done in the area of mechanics of hydrogels. First, in the area of modeling and simulation, more efforts can be devoted to develop more robust simulation tools to predict material response when exposed to a diverse array of external stimuli.

While much has been achieved in the modeling and simulation of hydrogels, there are seemingly less experimental works focusing on the characterization of mechanical behaviors of hydrogels.

The large deformation present in soft materials makes it an attractive material for replacement of traditional engineering materials. As seen in Sec. 6, there is a trend of machines moving away from hard engineering materials and taking the form of soft machines.

In materials engineering, stronger and better materials systems or composites are obtained when we combine materials of different properties. This notion of developing superior materials can also be extended to soft materials, such as gel and shape memory polymer (SMP) composite materials [He *et al.*, 2015]. Due to the excellent compatibility of hydrogel-based composites, and their enhanced deformation behavior and mechanical properties, more advanced combined materials are emerging especially in soft machine design.

As many issues related to the mechanics of hydrogel behaviors remain open, we list below some outlines for plausible future directions in the research of the mechanics of hydrogels.

(1) In the modeling and simulation of deformation behavior of hydrogel, more robust kinetic models and more robust subroutines which can simulate the diffusion mechanism of solvent molecules and ions over a long timeframe, as well as short timeframe effects, such as viscoelastic effects, needs to be further developed [Toh, 2015].
(2) It will be useful to develop a unified constitutive model for hydrogels deformation and to study the effects of various stimuli on the gel. This unified model can consider different stimuli, such as mechanical, temperature, photonics, chemical, electrical stimuli, as well as the coupling of different stimuli.
(3) Current study of phase transition phenomenon of hydrogels is limited to the equilibrium swelling state with homogenous dispersion of stimuli-induced

chemical reactions within the gel, such as photo-chemical reactions. However, the distribution of such chemical reactions in gels is never homogeneous. Therefore, it will be imperative to develop the models which can incorporate this inhomogeneity.

(4) Soft machines are mostly hybrids of soft and hard materials, for example devices based on the fabrication of islands consisting of stiff materials on polymer (hydrogel) substrates. In this design, many issues concerning the mechanics of hydrogels will emerge, such as the deformation compatibility of soft materials and hard materials and their interaction, as well as the contact and adhesion issues between the different materials. Therefore, the various deformation modes of wrinkling, twisting, buckling and necking of hydogels or combined hydrogels bilayers should be investigated further.

(5) Many parts of the human body are hydrogel-like in nature, and can be assumed to be mixtures of macromolecules and water. The meniscus is one such example, which can be repaired by using special hydrogels. Thus, the mechanics of hydrogels will become an important issue in biomechanics as hydrogels find more applications in the human body.

8. Conclusion

This paper has been written with the aim to consolidate ideas related to the mechanics of hydrogels: the theories developed, the phenomena associated and the applications. Both multiphase and monophase theories have been explored, with attention being cast more on the monophase theories for its unifying approach and relative ease of use in developing simulation models.

With better understanding of the mechanics of hydrogels, it is possible to develop novel applications which may possess superior performance over current conventional engineering materials. Furthermore, the similarity between hydrogel swelling and morphologies in nature allows us to make use of gel mechanics to gain a deeper insight into our natural world.

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