



Research paper

Constitutive equations for the kinetics of swelling of hydrogels



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ABSTRACT

Governing equations are reported for the kinetics of swelling of neutral gels subjected to finite deformations. Transport of solvent through a polymer network is described by the nonlinear diffusion equation with an equivalent diffusivity strongly affected by volume fraction of the solid phase. Material constants are determined by fitting observations in water uptake tests on NIPA, AAm and gelatin gels (taken from the literature) and HEMA gels (reported in this study) under unconstrained (spherical particles) and constrained (free-standing films and thin films attached to rigid substrates) swelling. Good agreement is demonstrated between the experimental swelling diagrams and results of simulation.

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1. Introduction

Hydrogels are three-dimensional networks of polymer chains connected by chemical and physical cross-links. Being immersed into water, a gel swells retaining structural integrity and the ability to withstand large deformations. The mechanical response of gels under swelling has recently attracted substantial attention as these materials demonstrate potential for a wide range of “smart” applications including biomedical devices, drug delivery carriers, scaffolds for tissue engineering, sensors, and soft actuators (Stuart et al., 2010; Koetting et al., 2015).

Studies on transient swelling of gels were initiated by Tanaka and Fillmore (1979), who investigated the kinetics of water uptake by a spherical gel particle. Li and Tanaka (1990) have shown that the kinetics of swelling is strongly affected by shape of a specimen: although the equilibrium degrees of swelling for a spherical particle and a thin disk coincide, the time needed for the disk to reach its equilibrium state exceeds the equilibration time for the spherical particle by an order of magnitude. A pronounced influence of geometrical constraints on water uptake by gels was demonstrated by (Yoon et al., 2010). Comparison of swelling processes for a free-standing layer and the same layer attached to a rigid substrate reveals that the presence of constraints results in a noticeable (by twice) growth of the equilibrium thickness and a strong (by several times) increase in time necessary to reach the equilibrium state. Transport of solvent molecules through a gel under constrained swelling–shrinking was studied in Liu et al. (2013), where it is shown that the rate of permeation increases substantially with degree of swelling.

The first model for the kinetics of water uptake by a spherical gel particle was developed by Tanaka and Fillmore (1979) based on a number of simplifications. This model was elaborated in Peters and Candau (1986), where the effect of shear modulus of the polymer network on transport of water molecules was taken into account. The Tanaka–Fillmore model was generalized for the analysis of swelling of non-spherical gels by Barriere and Leibler (2003); Yamaue and Doi (2004,2005), see Doi (2009) for a review. In these models, transport of solvent under swelling (a slow flow of water through a polymer network) is presumed to be governed by the equation

$$\zeta(\mathbf{v}_w - \mathbf{v}_n) = -\phi_w \nabla \Pi, \quad (1)$$

where \mathbf{v}_w , \mathbf{v}_n are velocity vectors for water and the network, Π stands for osmotic pressure, ∇ is the gradient operator, ϕ_w is volume fraction of water, and ζ is a coefficient of friction between water molecules and segments of chains. Eq. (1) expresses the balance between the drag force acting on solvent molecules and the gradient of osmotic pressure applied to the fluid phase. Combination of Eq. (1) with the equilibrium equation for stresses in the network and the molecular incompressibility condition results in a diffusion equation with an equivalent coefficient of diffusion inversely proportional to ζ . An advantage of this approach (the so-called linear theory of poroelasticity) is that it describes adequately the kinetics of water uptake under unconstrained and constrained swelling, and its conclusions (the time necessary for equilibration is inversely proportional to the square of the characteristic size of a sample) are confirmed experimentally (Peters and Candau, 1986; Suzuki and Hara, 2001). Two shortcomings of the linear theory of poroelasticity are to be mentioned (Yoon et al., 2010; Quesada-Perez et al., 2011; Bouklas and Huang, 2012): (i) it is confined to the analysis of swelling within the framework of small strains,

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while water uptake by a gel is accompanied by finite deformations, and (ii) the model does not involve the Flory–Huggins parameter, which means that it disregards interactions between water molecules and hydrophilic/hydrophobic segments of chains.

Several attempts have been undertaken to develop a concept of finite poroelasticity based on the mixing theory for interacting continua (Green and Adkins, 1964; Crochet and Naghdi, 1966; Shi et al., 1981; Zhang and Calderer, 2008; Baek and Pence, 2011) and the theory of fluid transport through porous media (Bennethum and Cushman, 1996; Singh et al., 2003; Weinstein and Bennethum, 2006), see Rajagopal (2003) for review. To the best of our knowledge, none of these models has been verified by comparison with experimental data in swelling tests on gels.

Another approach to the description of swelling of hydrogels is grounded on treatment of transport of solvent as diffusion of water molecules through a gel and application of the Flory theory of swelling (Flory, 1953). A constitutive framework for the analysis of transient water uptake at finite deformations was developed by Hong et al. (2008); Duda et al. (2010); Chester and Anand (2010); Drozdov and Christiansen (2013a); Lucantonio et al. (2013), to mention a few. An advantage of this concept is that constitutive equations involve a small number of adjustable parameters, which allows results of simulation to be compared with experimental data. Its shortcoming is that the diffusivity of water molecules cannot be treated as a constant: observations in water uptake tests reveal that the model underestimates strongly (by an order of magnitude) degree of swelling when the maximum diffusivity of water molecules (the coefficient of self-diffusion) is used in calculations (Engelsberg and Barros, 2013). This requires an extra equation to be introduced that describes an increase in diffusivity D with concentration of water molecules c . Conventionally, D is presumed to be proportional to c (Lucantonio et al., 2013) or to c^n with n treated as an adjustable parameter (Baek and Srinivasa, 2004; Duda et al., 2010; Chester and Anand, 2010), see Amsden (1998) and Masaro and Zhu (1999) for a discussion of phenomenological relations between D and c . Although these relations lead to reasonable qualitative predictions, they have not yet been validated quantitatively by comparison with experimental data.

The objective of this study is (i) to establish correlation between the flux of water molecules in the diffusion concept for solvent transport and friction of water molecules and segments of chains in the concept of linear poroelasticity, (ii) to derive an expression for diffusivity that is grounded on experimental data for the growth of molecular friction with volume fraction of polymer network, and (iii) to validate this expression by comparison of results of simulation with observations in swelling tests.

The exposition is organized as follows. Governing equations for the elastic response of a gel and transport of water molecules are discussed in Section 2. These relations are applied to the analysis of swelling-induced deformation of a free-standing film and a film attached to a substrate in Section 3. Unconstrained swelling of spherical particles is analyzed in Section 4. Experimental data in mechanical tests (tension with a constant strain rate, relaxation, and cyclic loading of swollen specimens) and swelling tests on HEMA gels with two mass fractions on monomers in pre-gel solutions are reported in Section 5, where the observations are approximated by the model. Concluding remarks are formulated in Section 6.

2. Governing equations

A gel is treated as a two-phase medium composed of solid (a polymer network) and fluid (water) constituents. The solid and fluid phases are modeled as immiscible (mass exchange between the phases is disregarded) inter-penetrating continua (any elementary volume contains both phases).

Deformation of a gel coincides with that of its polymer network. It is convenient to introduce a special state of an undeformed dry gel. This state will be called the initial state in what follows (the name is used by tradition, it is not presumed that a gel occupies this state at some “initial” instant). Transformation of the initial state into the actual state is described by the deformation gradient \mathbf{F} . Under some experimental programs, the initial state is real (for example, when an as-prepared gel is dried, and the dry sample is subjected to water uptake). Under other programs, this state is fictitious and it is not realized in tests (for example when an as-prepared gel is directly immersed into a water bath for swelling).

Denote by C concentration of water molecules (number of molecules per unit volume in the initial state). We adopt the molecular incompressibility condition

$$J = 1 + Cv, \quad J = \det \mathbf{F}, \quad (2)$$

where v stands for the characteristic volume of a water molecule. According to Eq. (2), volume deformation of a gel is driven by changes in concentration of water only. Concentration of water molecules per unit volume in the actual configuration reads

$$c = \frac{C}{J}. \quad (3)$$

The reference state of the polymer network (in which stresses in chain vanish) coincides with its as-prepared state (where cross-linking polymerization of monomers is performed), but it can differ from the initial state. Transformation of the initial configuration into the reference configuration is described by the deformation gradient

$$\mathbf{f} = f^{\frac{1}{3}} \mathbf{I}, \quad (4)$$

where f is the coefficient of inflation under transition from the dry state to the as-prepared state, and \mathbf{I} stands for the unit tensor.

According to the multiplicative decomposition formula, the deformation gradient \mathbf{F} for transition from the initial configuration to the actual configuration reads

$$\mathbf{F} = \mathbf{F}_e \cdot \mathbf{f}, \quad (5)$$

where \mathbf{F}_e denotes the deformation gradient for elastic deformation, and the dot stands for inner product. Combination of Eqs. (4) and (5) implies that

$$\mathbf{F} = f^{\frac{1}{3}} \mathbf{F}_e. \quad (6)$$

The Cauchy–Green tensors for elastic deformation are given by

$$\mathbf{B}_e = \mathbf{F}_e \cdot \mathbf{F}_e^{\top}, \quad \mathbf{C}_e = \mathbf{F}_e^{\top} \cdot \mathbf{F}_e, \quad (7)$$

where \top stands for transpose. These tensors are connected with the Cauchy–Green tensors for macro-deformation

$$\mathbf{B} = \mathbf{F} \cdot \mathbf{F}^{\top}, \quad \mathbf{C} = \mathbf{F}^{\top} \cdot \mathbf{F} \quad (8)$$

by the formulas

$$\mathbf{B}_e = f^{-\frac{2}{3}} \mathbf{B}, \quad \mathbf{C}_e = f^{-\frac{2}{3}} \mathbf{C}. \quad (9)$$

Transport of water molecules is modeled as its diffusion through the polymer network governed by the equation

$$\mathbf{j} = -\frac{Dc}{k_B T} \nabla \mu, \quad (10)$$

where \mathbf{j} and ∇ are the flux vector and the gradient operator in the actual configuration, μ is the chemical potential of water molecules, D stands for diffusivity, k_B is Boltzmann’s constant, and T denotes absolute temperature. It follows from Eqs. (2), (3), (10) that

$$\mathbf{j}_0 = -\frac{DC}{k_B T} \mathbf{F}^{-1} \cdot \nabla_0 \mu \cdot \mathbf{F}^{-1}, \quad (11)$$

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