

# KINETICS OF SWELLING GELS

JAMES P. KEENER\*, SARTHOK SIRCAR AND AARON L. FOGELSON\*  
DEPARTMENTS OF MATHEMATICS AND BIOENGINEERING\*  
UNIVERSITY OF UTAH  
SALT LAKE CITY, UT 84112

**Abstract.** We develop a general theory of the swelling kinetics of polymer gels, with the view that a polymer gel is a two-phase fluid. The model we propose is a free boundary problem and can be used to understand both contraction and swelling, including complete dissolving or dehydration of polymeric gels. We show that the equations of motion satisfy a minimum energy dissipation rate principle similar to the Helmholtz minimum dissipation rate principle which holds for a Stokes' flow. We also show, using asymptotic analysis and numerical simulation, how the equilibrium swelled state and the swelling rate constant are related to the free energy and rheological properties of the polymer network.

**Acknowledgment:** This research was supported in part by NSF grant DMS-0540779 and NIGMS grant R01-GM090203.

**Key words:** swelling kinetics, gel diffusivity, moving boundary, free energy.

**1. Introduction.** The theory to understand the swelling and deswelling of gels has a long history beginning with the classical work of Flory [6, 8, 9] and Katchalsky [14]. (see also [4, 7]) In this theory, the free energy is used to make predictions about the thermodynamical equilibrium configurations of polymer gels and their dependence on environmental parameters such as temperature or solvent ion concentrations.

An important problem is to understand how the kinetics (and not simply the equilibria) of swelling and deswelling is governed. An early answer was given by Tanaka and colleagues [25, 26] who developed a kinetic theory of swelling gels viewing a gel as a linear elastic solid immersed in a viscous fluid. Although they neglected the motion of the fluid solvent, the model reasonably explained the swelling of a gel to its equilibrium volume fraction.

This early work gave rise to the concept of gel diffusivity as a way to characterize the kinetics of swelling. The gel diffusivity is defined as  $D = \frac{aL^2}{\tau}$  where  $L$  is the equilibrium size (length or radius) of a gel and  $\tau$  is the time constant of exponential swelling toward the equilibrium size. The dimensionless scale factor  $a$  is related to the geometry of the gel. They found that expansion of the gel was governed approximately by a diffusion equation with diffusion coefficient  $D$ . However, how the diffusivity of the gel, or more generally the kinetics of swelling (perhaps with large changes in volume fraction) is affected by the free energy is less well understood.

Subsequent studies relaxed the assumption of linear elasticity by defining the force on the gel to be the functional derivative of the free energy function for the polymer mesh [5, 19, 22, 24, 31]. However, most of these works neglected the fluid flow that must accompany swelling. Wang et al. [27] added fluid flow by application of two-phase flow theory but considered only small polymer volume fractions and small gradients in the volume fraction. Durning and Morman [5] also used continuity equations to describe the flow of solvent and solution in the gel, but used a diffusion approximation with a constant diffusion coefficient to determine the fluid motion. More recently, Wolgemuth et al. [29] extended these theories to study the swelling of a polyelectrolyte gel.

Multiphase fluid models have been used to study a number of important physical and biological problems with connections to gel swelling. These include cartilage mechanics [13, 17, 16, 11], the contraction of actin-myosin networks [12, 23], the propulsion of myxobacteria via swelling of slime [28, 30] and biofilm formation [2, 32, 33].

A main problem considered by all of these works is to understand how the various physical and chemical forces within the gel result in motions of swelling and deswelling.

The purpose of this paper is to give a two-phase fluid model of gel swelling that incorporates the free energy thereby giving an improved understanding of how the nonlinear kinetics of swelling of a gel are influenced by the free energy and the rheological properties of the gel.

The experiment we have in mind is as follows. A polymer gel is at equilibrium, when suddenly the environment is changed. This could be the result of a change of temperature or the concentration of some significant chemical species (as happens when you swallow a gel capsule pill). Because of this change of environment, the gel is no longer at equilibrium and will swell (hydrate) or condense (dehydrate) to bring it to its new equilibrium state. It may swell without bound (dissolve) or it may approach a new equilibrium

concentration and radius.

In what follows we derive equations describing the kinetics of a polymer gel, provide a variety of analyses of these equations and show numerical solutions of these equations in different parameter regimes.

**2. Model Description.** A gel is comprised of a polymer network in a solvent containing a variety of ionic species. We model this gel as a two-phase material consisting of constant density polymer and solvent phases, with volume fractions  $(\theta_p, \theta_s)$  which move with velocity  $(\mathbf{v}_p, \mathbf{v}_s)$ , respectively, [20, 21]. Because there is no interconversion between polymer and solvent, each of the two species satisfy a conservation law. The transport equation for polymer network  $\theta_p$  is given by

$$\frac{\partial \theta_p}{\partial t} + \nabla \cdot (\theta_p \mathbf{v}_p) = 0, \quad (2.1)$$

and the transport of solvent  $\theta_s$  is described by

$$\frac{\partial \theta_s}{\partial t} + \nabla \cdot (\theta_s \mathbf{v}_s) = 0, \quad (2.2)$$

Since

$$\theta_p + \theta_s = 1, \quad (2.3)$$

it must be that

$$\nabla \cdot \mathbf{v} = 0, \quad (2.4)$$

where  $\mathbf{v} = \theta_p \mathbf{v}_p + \theta_s \mathbf{v}_s$  is the volume-average velocity of the system.

**2.1. Force Balance.** We consider the situation in which inertial effects can be ignored. The force balance equations are

$$\nabla \cdot (\theta_p \sigma_p) - \xi \theta_p \theta_s (\mathbf{v}_p - \mathbf{v}_s) - \theta_p \nabla \mu_p - \theta_p \nabla P = 0, \quad (2.5)$$

for the polymer network and

$$\nabla \cdot (\theta_s \sigma_s) - \xi \theta_p \theta_s (\mathbf{v}_s - \mathbf{v}_p) - \theta_s \nabla \mu_s - \theta_s \nabla P = 0, \quad (2.6)$$

for the solvent. Here  $\sigma_j$ ,  $j = p, s$ , are the stress tensors, the term  $\xi \theta_s \theta_p (\mathbf{v}_p - \mathbf{v}_s)$  describes the drag between the polymer network and the solvent,  $\theta_j \nabla \mu_j$ ,  $j = p, s$ , are forces due to the chemical potentials, and  $\theta_j \nabla P$ ,  $j = p, s$ , are the forces due to hydrostatic pressure gradient, required in order to enforce the incompressibility condition (2.4).

The solvent stress tensor  $\sigma_s$  is taken to be that for a Newtonian fluid. The polymer stress tensor  $\sigma_p$  can include viscous, elastic or visco-elastic contributions, arising, for example, from permanent bonds between polymer strands or the effect of entanglements amongst polymer strands. For this paper, we consider a polymer with no permanent cross-linking bonds (hence no elastic stresses). This assumption is appropriate for many biological gels, such as mucus. While entanglements are important in such gels, we postpone treatment of these and other viscoelastic effects to future work. Hence, the stress tensors have the form  $\sigma_j = \frac{1}{2} \eta_j (\nabla \mathbf{v}_j + \nabla \mathbf{v}_j^T) + \lambda_j \mathbf{I} \nabla \cdot \mathbf{v}_j$ ,  $j = p, s$ . For reasons described below, we require the viscosities to satisfy  $\eta_j > 0$  and  $\eta_j + 3\lambda_j > 0$ .

**2.2. Chemical Potential.** The chemical pressure terms in the force balance equations are defined as follows: We let  $f(\theta_p)$  be the total free energy density. This could include, for example, terms involving entropy, polymer-solvent interaction energy, and coulombic interaction energy between ions and charges on the polymer.

The solvent chemical potential is the change in energy following addition of a solvent molecule to a volume of the gel mixture, and the polymer chemical potential is the change of energy following addition of a molecule of polymer to the gel volume. It follows [3] that the solvent chemical potential density is

$$\mu_s = f - \theta_p \frac{\partial f}{\partial \theta_p}, \quad (2.7)$$

and the polymer chemical potential density is

$$\mu_p = f + \theta_s \frac{\partial f}{\partial \theta_p}. \quad (2.8)$$

There are two identities that are immediate. The first is

$$\theta_p \mu_p + \theta_s \mu_s = f, \quad (2.9)$$

known as the *Gibbs-Duhem relationship* and the second is

$$\mu_p - \mu_s = \frac{\partial f}{\partial \theta_p}, \quad (2.10)$$

so that  $\mu_p = \mu_s$  (i.e., chemical potentials are in balance) at extremal points of  $f$ .

Now, the force that the solvent exerts on the polymer is  $-\theta_p \nabla \mu_p$  and the force exerted on the solvent by the polymer network is  $-\theta_s \nabla \mu_s$ . The sum of these two forces is

$$-\theta_p \nabla \mu_p - \theta_s \nabla \mu_s = \left( -\frac{\partial}{\partial \theta_p} (\theta_p \mu_p + \theta_s \mu_s) + (\mu_p - \mu_s) \right) \nabla \theta_p = 0, \quad (2.11)$$

because of (2.9) and (2.10). In other words, the force exerted on the polymer by the solvent is equal and opposite to the force exerted on the solvent by the polymer, which, according to Newton's third law, is required. In many treatments of two phase fluids, only the polymer chemical potential  $\mu_p$  is included in the force balance equations.

**2.3. Minimum Energy Dissipation Rate Principle.** In this section, we generalize the argument of Helmholtz [1, 10, 18] for a Stokes flow to show that the flow specified by the force balance equations (2.5) and (2.6), along with appropriate interface conditions, minimizes the rate of energy dissipation.

Suppose that  $\Omega$  is a fixed domain inside of which there is polymer and solvent. On the boundary of  $\Omega$ , the velocities are taken to be fixed. However, there may be an interface, a surface  $\Gamma$  contained in  $\Omega$ , across which  $\theta_p$  is discontinuous. The functional

$$D_E = \int_{\Omega} \left( \frac{1}{2} \theta_p \sigma_p(\mathbf{V}_p) : \varepsilon(\mathbf{V}_p) + \frac{1}{2} \theta_s \sigma_s(\mathbf{V}_s) : \varepsilon(\mathbf{V}_s) + \frac{1}{2} \xi \theta_p \theta_s (\mathbf{V}_p - \mathbf{V}_s)^2 - \mu_p \nabla \cdot (\theta_p \mathbf{V}_p) - \mu_s \nabla \cdot (\theta_s \mathbf{V}_s) \right) dV, \quad (2.12)$$

is the total rate of energy dissipation for the flow with velocities  $\mathbf{V}_p, \mathbf{V}_s$ . Here  $\varepsilon(\mathbf{v}) = \frac{1}{2}(\nabla \mathbf{v} + \nabla \mathbf{v}^T)$ ,  $\sigma_j(\mathbf{v}) = \eta_j \varepsilon(\mathbf{v}) + \lambda_j I \nabla \cdot \mathbf{v}$ , where  $\eta_j > 0$  and  $\lambda_j$ ,  $j = p, s$ , are the viscosities. Thus, the first two terms in  $D_E$  represent the rate of energy dissipated by viscosity in the polymer and solvent. The third term represents the energy dissipation rate due to drag between the two materials. The term  $\mu_p \nabla \cdot (\theta_p \mathbf{V}_p)$  corresponds to the rate of work required to compress polymer network and the term  $\mu_s \nabla \cdot (\theta_s \mathbf{V}_s)$  corresponds to the rate of work required to compress solvent.

We wish to find the flow that minimizes the energy dissipation rate  $D_E$ , subject to the incompressibility condition (2.4). Accordingly, we seek to minimize the functional

$$F_E = D_E - \int_{\Omega} P \nabla \cdot (\theta_p \mathbf{V}_p + \theta_s \mathbf{V}_s) dV \quad (2.13)$$

over all admissible functions  $(\mathbf{V}_p, \mathbf{V}_s, P)$ . Here,  $P$  is the Lagrange multiplier used to enforce incompressibility.

Functions for which the first variation of  $F_E$  is zero are minimizers of  $F_E$ . This follows since  $F_E$  is a convex functional. In particular, the operator

$$\sigma_j(\mathbf{V}_j) : \varepsilon(\mathbf{V}_j) \equiv \eta_j \varepsilon(\mathbf{V}_j) : \varepsilon(\mathbf{V}_j) + \lambda_j (\nabla \cdot \mathbf{V}_j)^2 \quad (2.14)$$

is a positive definite quadratic function of  $\nabla \mathbf{V}_j$ , provided  $\eta_j > 0$  and  $\eta_j + 3\lambda_j > 0$ .

Functions  $\mathbf{V}_p$  and  $\mathbf{V}_s$  are admissible if they are differentiable and specified on the boundary of  $\Omega$  and if  $\nabla \cdot (\theta_p \mathbf{V}_p + \theta_s \mathbf{V}_s)$  is well-defined. The Euler-Lagrange equations are calculated in the standard way: We let

a perturbation be given by  $(\mathbf{V}_p + \epsilon \mathbf{v}_p, \mathbf{V}_s + \epsilon \mathbf{v}_s)$ . Then we require that the first variation, equivalently the derivative of  $F_E$  with respect to  $\epsilon$  at  $\epsilon = 0$ , be zero,

$$0 = \int_{\Omega} \left( \sum_{j=s,p} (\theta_j \eta_j \varepsilon(\mathbf{V}_j) : \varepsilon(\mathbf{v}_j) + \theta_j \lambda_j (\nabla \cdot \mathbf{V}_j) (\nabla \cdot \mathbf{v}_j)) + \xi \theta_p \theta_s (\mathbf{V}_p - \mathbf{V}_s) (\mathbf{v}_p - \mathbf{v}_s) - \mu_p \nabla \cdot (\theta_p \mathbf{v}_p) - \mu_s \nabla \cdot (\theta_s \mathbf{v}_s) - P \nabla \cdot (\theta_p \mathbf{v}_p + \theta_s \mathbf{v}_s) \right) dV. \quad (2.15)$$

The symmetry of  $\varepsilon(\mathbf{V})$  implies that  $\varepsilon(\mathbf{V}) : \varepsilon(\mathbf{v}) = \varepsilon(\mathbf{V}) : \nabla \mathbf{v}$ , and we can rewrite (2.15) as

$$0 = \int_{\Omega} (\theta_p \eta_p \varepsilon(\mathbf{V}_p) : \nabla \mathbf{v}_p + \theta_p \lambda_p (\nabla \cdot \mathbf{V}_p) (\nabla \cdot \mathbf{v}_p) + \xi \theta_p \theta_s (\mathbf{V}_p - \mathbf{V}_s) \mathbf{v}_p - \mu_p \nabla \cdot (\theta_p \mathbf{v}_p) - P \nabla \cdot (\theta_p \mathbf{v}_p)) dV + \int_{\Omega} (\theta_s \eta_s \varepsilon(\mathbf{V}_s) : \nabla \mathbf{v}_s + \theta_s \lambda_s (\nabla \cdot \mathbf{V}_s) (\nabla \cdot \mathbf{v}_s) - \xi \theta_p \theta_s (\mathbf{V}_p - \mathbf{V}_s) \mathbf{v}_s - \mu_s \nabla \cdot (\theta_s \mathbf{v}_s) - P \nabla \cdot (\theta_s \mathbf{v}_s)) dV.$$

Now apply the divergence theorem to find

$$0 = \int_{\Omega} (-\nabla \cdot (\theta_p \sigma_p(\mathbf{V}_p)) + \xi \theta_p \theta_s (\mathbf{V}_p - \mathbf{V}_s) + \theta_p \nabla \mu_p + \theta_p \nabla P) \mathbf{v}_p dV + \int_{\Omega} (-\nabla \cdot (\theta_s \sigma_s(\mathbf{V}_s)) - \xi \theta_p \theta_s (\mathbf{V}_p - \mathbf{V}_s) + \theta_s \nabla \mu_s + \theta_s \nabla P) \mathbf{v}_s dV + \int_{\Gamma} [\theta_p e_p \mathbf{v}_p + \theta_s e_s \mathbf{v}_s] dS,$$

where  $e_j \mathbf{v}_j = \sigma_j(\mathbf{V}_j) : \mathbf{n} \mathbf{v}_j - P \mathbf{n} \cdot \mathbf{v}_j - \mu_j \mathbf{n} \cdot \mathbf{v}_j$  with subscripts  $j = p, s$ ;  $\mathbf{n}$  is the outward unit normal vector at the interface  $\Gamma$ ; and by  $[g]$ , we mean the jump in the quantity  $g$  across  $\Gamma$ . The terms involving  $\nabla \cdot \mathbf{v}_j$  vanish because  $\mathbf{v}_j = 0$  on the boundary of  $\Omega$ .

Treating  $\mathbf{v}_p$  and  $\mathbf{v}_s$  on the interior of  $\Omega$  as independent and arbitrary, we find the force balance equations (2.5) and (2.6) as above.

Although the individual velocities need not be continuous across the interface,  $\theta_p \mathbf{V}_p + \theta_s \mathbf{V}_s$  must be a continuous function, and the variations must satisfy the constraint  $[\theta_p \mathbf{v}_p + \theta_s \mathbf{v}_s] = 0$  on  $\Gamma$ . Thus, on  $\Gamma$ , there are only three independent variations possible. It follows that we must have

$$0 = (\theta_p^- e_p^- - \theta_p^- e_s^+) \mathbf{v}_p^- + (\theta_s^- e_s^- - \theta_s^- e_s^+) \mathbf{v}_s^- - (\theta_p^+ e_p^+ - \theta_p^+ e_s^+) \mathbf{v}_p^+, \quad (2.16)$$

or

$$e_p^- = e_s^+, \quad e_s^- = e_s^+, \quad (2.17)$$

and

$$e_p^+ = e_s^+, \quad (2.18)$$

if  $\theta_p^+ \neq 0$ . (We assume that  $\theta_p^- \neq 0$ ).

In the case that there is an edge to the gel, on one side of which (inside the gel)  $\theta_p = \theta_p^-$ , and on the other side of which (outside the gel)  $\theta_p = 0$ ,  $\theta_s = 1$ , the interface conditions (2.17) reduce to

$$\sigma_p^- \mathbf{n} - \sigma_s^- \mathbf{n} = \frac{\partial f}{\partial \theta_p} \mathbf{n}, \quad (2.19)$$

where we have used (2.10). Because these are consistent with the minimum energy dissipation rate principle, we take these to be the interface conditions for the gel.

### 3. Analysis of the Model Equations.

**3.1. Non-Dimensionalization.** We first non-dimensionalize the equations of motion (2.1,2.2,2.5,2.6), and the interface condition (2.19). To this end we let  $\tau$  be a characteristic time and  $l$  be a characteristic length, and then rescale space and time by these characteristic scales. Next observe that a characteristic scale for the free energy density function  $f$  is  $\frac{k_B T}{\nu_m}$ , where  $\nu_m$  is a characteristic volume of a monomeric unit. Thus, by introducing the change of variables

$$\hat{\mathbf{v}}_j = \frac{\tau}{l} \mathbf{v}_j, \quad \hat{\mu}_j = \frac{\nu_m}{k_b T} \mu_j, \quad \hat{\eta}_j = \frac{\nu_m}{l^2 k_b T \tau} \eta_j, \quad \hat{\lambda}_j = \frac{\nu_m}{l^2 k_b T \tau} \lambda_j, \quad (3.1)$$

for  $j = p, s$  and

$$\hat{\xi} = \frac{\nu_m}{k_b T} \xi, \quad (3.2)$$

and then dropping the  $\hat{\cdot}$ , we arrive at exactly the same governing equations in dimensionless units of space and time. While at first glance this appears to be of little consequence, it is actually quite significant because it implies that for small gels  $\eta_j \gg \xi$  while for large gels the opposite  $\eta_j \ll \xi$  is true. That is, the swelling of small gels is viscosity dominated while the swelling of large gels is drag dominated. As we demonstrate below, this has consequences for how the gel swells.

**3.2. Steady state solutions.** Steady solutions occur when there is no movement. If there is no movement, then velocities are zero, in which case, at the interface

$$\frac{\partial f}{\partial \theta_p} = 0. \quad (3.3)$$

Furthermore, if velocities are zero in the interior, then it follows from (2.5) and (2.6) that

$$\nabla(\mu_p - \mu_s) = f''(\theta_p) \nabla \theta_p = 0. \quad (3.4)$$

(Here and below we use the notation  $f' = \frac{\partial f}{\partial \theta_p}$  and  $f'' = \frac{\partial^2 f}{\partial \theta_p^2}$ .) In other words, the equilibria of this system are uniform in space with  $\theta_p$  at the extremal values of the energy density function  $f$ . If no such equilibria exist, the expectation is that the gel will either dehydrate ( $\theta_p \rightarrow 1$ ), excluding all the solvent, or will swell to infinite size, i.e., dissolve ( $\theta_p \rightarrow 0$ ).

**3.3. One-dimensional gels.** We now consider the swelling dynamics of a one-dimensional gel. A significant challenge to understanding the swelling kinetics of a gel comes from the fact that this is a moving boundary problem. In one spatial dimension, this problem is simplified greatly and much can be done to understand the kinetics of swelling.

A one-dimensional gel is one for which  $\theta_p$  is non-zero on the domain  $0 < x < L$ , with  $L$  a function of time. We assume that there is a wall at  $x = 0$ , so that  $v_p = v_s = 0$  at  $x = 0$ . This also implies that  $\theta_p v_p + \theta_s v_s = 0$  throughout the domain. Because polymer is conserved, i.e., neither created nor destroyed, the velocity of the moving boundary must be the same as the gel velocity at the boundary,

$$\frac{dL}{dt} = v_p(L). \quad (3.5)$$

In one spatial dimension, the conservation law becomes

$$\frac{\partial \theta_p}{\partial t} + \frac{\partial}{\partial x} (v_p \theta_p) = 0, \quad (3.6)$$

and the force balance reduces to the single equation

$$\eta'_p \theta_s \frac{\partial}{\partial x} \left( \theta_p \frac{\partial v_p}{\partial x} \right) + \eta'_s \theta_p \frac{\partial}{\partial x} \left( \theta_s \frac{\partial \theta_p v_p}{\partial x} \right) - \xi \theta_p v_p - \theta_p \theta_s f''(\theta_p) \frac{\partial \theta_p}{\partial x} = 0, \quad (3.7)$$

subject to the boundary condition

$$\frac{\partial}{\partial x} \left( \eta'_p v_p + \eta'_s \left( \frac{\theta_p v_p}{\theta_s} \right) \right) = f'(\theta_p), \quad (3.8)$$

at  $x = L$  and  $v_p = 0$  at  $x = 0$ . Here the viscosities are  $\eta'_j = \eta_j + \lambda_j$ , however, in what follows, we drop the '.

Since this is a moving boundary problem, it is convenient to map the domain  $0 < x < L(t)$  onto the fixed domain  $0 < y < 1$  by making the change of variables  $x = L(\tau)y$  and  $t = \tau$ . Using the chain rule, we find that

$$\frac{\partial}{\partial x} = \frac{1}{L} \frac{\partial}{\partial y}, \quad \frac{\partial}{\partial t} = \frac{\partial}{\partial \tau} - \frac{yL'}{L} \frac{\partial}{\partial y}.$$

Using these, we write (3.6) as

$$\frac{\partial \theta_p}{\partial \tau} = \frac{yL'}{L} \frac{\partial \theta_p}{\partial y} - \frac{1}{L} \frac{\partial}{\partial y} (v_p \theta_p). \quad (3.9)$$

Multiply this by  $L$  and use the identity

$$\frac{\partial Ly}{\partial \tau} = L \frac{\partial y}{\partial \tau} + L' y,$$

to get

$$\frac{\partial (L\theta_p)}{\partial \tau} = - \frac{\partial}{\partial y} \left( \left\{ \frac{v_p}{L} - \frac{y v_p(1)}{L} \right\} (L\theta_p) \right), \quad (3.10)$$

for  $0 \leq y \leq 1$ . Notice that in this coordinate system  $L \int_0^1 \theta_p dy$  is a constant, independent of time.

Applying the same change of variables to the force balance equation (3.7) yields

$$\eta_p \theta_s \frac{\partial}{\partial y} \left( \theta_p \frac{\partial v_p}{\partial y} \right) + \eta_s \theta_p \frac{\partial}{\partial y} \left( \theta_s \frac{\partial \theta_p v_p}{\partial y} \right) - \xi L^2 \theta_p v_p - L \theta_p \theta_s f''(\theta_p) \frac{\partial \theta_p}{\partial y} = 0, \quad (3.11)$$

subject to boundary conditions

$$\frac{\partial}{\partial y} \left( \eta_p v_p + \eta_s \left( \frac{\theta_p v_p}{\theta_s} \right) \right) = L f'(\theta_p), \quad (3.12)$$

at  $y = 1$  and  $v_p(0) = 0$ . Here we have taken

$$\frac{dL}{d\tau} = v_p(y = 1). \quad (3.13)$$

**3.4. Reduced Solution 1:  $\xi = 0$  (No Drag).** We can find an exact solution to this problem in the case that there is no drag ( $\xi = 0$ ). Suppose that  $\theta_p$  is constant in space. Then the force balance equation (3.11) reduces to

$$\eta_e \theta_p \frac{\partial^2 v_p}{\partial y^2} = 0, \quad (3.14)$$

where  $\eta_e = \eta_p \theta_s + \eta_s \theta_p$ . It follows that  $v_p$  is a linear function of space  $v_p = u_p Ly$ . Furthermore, the boundary condition (3.12) implies that

$$u_p = \frac{\theta_s}{\eta_e} f'(\theta_p). \quad (3.15)$$

Finally, according to the conservation law (3.10),  $\frac{d}{d\tau} (L\theta_p) = 0$ , or

$$\frac{d\theta_p}{d\tau} = -u_p \theta_p = - \frac{\theta_s \theta_p f'(\theta_p)}{\eta_e}. \quad (3.16)$$

The solution of this first order differential equation is easy to understand. Notice that if  $f$  has an interior minimum at  $\theta_p^*$ , the solution will evolve toward this as an exponential with time constant

$$\tau_p = \frac{\eta_e^*}{\theta_p^* \theta_s^* f''(\theta_p^*)}. \quad (3.17)$$

However, if  $f$  is monotone decreasing, then the gel will dehydrate ( $\theta_p \rightarrow 1$ ) exponentially with time constant

$$\tau_p = -\frac{\eta_s}{f'(1)}. \quad (3.18)$$

On the other hand, if  $f$  is monotone increasing, the gel will dissolve ( $\theta_p \rightarrow 0$ ) with time constant

$$\tau_p = \frac{\eta_p}{f'(0)}. \quad (3.19)$$

A significant observation from this analysis is that the expansion/contraction rate of this gel shows no size dependence, in contrast to the result of Tanaka and Fillmore [25].

**3.5. Reduced Solution 2:  $\eta_p = \eta_s = 0$  (No Viscosity).** We suppose that  $\eta_p, \eta_s \ll \xi$ , which is correct if the gel is sufficiently large. In this limit (i.e., setting  $\eta_p = \eta_s = 0$ ), and with  $\theta_p v_p + \theta_s v_s = 0$ , we find from (3.7) that

$$\xi v_p = -\theta_s f''(\theta_p) \frac{\partial \theta_p}{\partial x}. \quad (3.20)$$

It follows that the evolution of  $\theta_p$  is governed by

$$\frac{\partial \theta_p}{\partial t} = \frac{1}{\xi} \frac{\partial}{\partial x} \left( \theta_s \theta_p f''(\theta_p) \frac{\partial \theta_p}{\partial x} \right), \quad (3.21)$$

a diffusion equation for  $\theta_p$ , however, on a domain with a moving boundary. The interface condition reduces to the Dirichlet boundary condition on  $\theta_p$ , namely

$$f'(\theta_p) = 0. \quad (3.22)$$

However, if the free energy does not have an interior minimum, then this condition is replaced by the Dirichlet condition  $\theta_p = 0$  if  $f$  is a monotone increasing function, or  $\theta_p = 1$  if  $f$  is monotone decreasing.

The interface moves with normal velocity

$$v_p = -\frac{1}{\xi} \theta_s f''(\theta_p) \frac{\partial \theta_p}{\partial x} \Big|_{x=L}. \quad (3.23)$$

In a fixed coordinate system, we end up with the diffusion advection equation on a fixed domain  $0 < y < 1$

$$\frac{\partial(L\theta_p)}{\partial \tau} = \frac{1}{L} \frac{\partial}{\partial y} \left( \left\{ \frac{1}{\xi} \theta_s f''(\theta_p) \frac{\partial \theta_p}{\partial y} - y \frac{dL}{d\tau} \right\} (L\theta_p) \right), \quad (3.24)$$

with

$$\frac{dL}{d\tau} = -\frac{1}{\xi L} \left( \theta_s f''(\theta_p) \frac{\partial \theta_p}{\partial y} \right) \Big|_{y=1}, \quad (3.25)$$

subject to boundary conditions  $\frac{\partial \theta_p}{\partial x} = 0$  at  $y = 0$  and  $f'(\theta_p) = 0$  at  $y = 1$ .

Below we show that if  $\theta_p^*$  is the equilibrium solution, then  $\theta_p$  equilibrates to  $\theta_p^*$  exponentially with the time constant

$$\tau_p = \frac{1}{\theta_p^* \theta_s^* f''(\theta_p^*)} \frac{\xi L^2}{\omega^2}, \quad (3.26)$$

where  $\omega$  is the smallest root of the equation  $\cos(\omega) = 0$ , i.e.,  $\omega = \frac{\pi}{2}$ . Here we see the size dependence predicted by the Tanaka and Fillmore theory [25], namely, that  $\frac{\tau_p}{L^2}$  is a constant.

**3.6. Perturbation Argument:  $\xi$  Small.** The fact that the solution is known for  $\xi = 0$  suggests that a perturbation argument may be possible. We begin with the force balance equation (3.11). We assume that  $\theta_p = \theta_p^0 + \xi\theta_1$ , where  $\theta_p^0$  is the mean value of  $\theta_p$ , constant in space, but not necessarily in time and  $\int_0^1 \theta_1 dy = 0$ . We also assume that  $v_p = u_p Ly + \xi v_1$ . To satisfy the boundary condition (3.12) to leading order in  $\xi$ , it must be that

$$\eta_e^0 u_p = \theta_s^0 f'(\theta_p^0). \quad (3.27)$$

We expand the force balance equation, getting to first order in  $\xi$ ,

$$\eta_e^0 \theta_p^0 \frac{\partial^2 v_1}{\partial y^2} + \eta_s \frac{\theta_p^0}{\theta_s^0} L u_p \frac{\partial^2}{\partial y^2} (y\theta_1) + L \eta_e^0 C_0 \frac{\partial \theta_1}{\partial y} - L^3 \theta_p^0 u_p y = 0, \quad (3.28)$$

where

$$\eta_e^0 C_0 = \eta_e^0 u_p - \eta_s u_p \frac{\theta_p^0}{\theta_s^0} - \theta_p^0 \theta_s^0 f''(\theta_p^0), \quad (3.29)$$

with boundary condition

$$\eta_e^0 \frac{\partial v_1}{\partial y} \Big|_{y=1} + L \eta_s \frac{u_p}{\theta_s^0} \frac{\partial}{\partial y} (y\theta_1) \Big|_{y=1} = L \theta_s^0 f''(\theta_p^0) \theta_1 \Big|_{y=1}. \quad (3.30)$$

We can integrate (3.28) to get

$$\eta_e^0 \theta_p^0 \frac{\partial v_1}{\partial y} + L \eta_s \frac{\theta_p^0}{\theta_s^0} u_p \frac{\partial}{\partial y} (y\theta_1) + L \eta_e^0 C_0 \theta_1 - \frac{L^3}{2} \theta_p^0 u_p y^2 = L \eta_e^0 C_1, \quad (3.31)$$

where  $C_1$  is determined from the boundary condition (3.30) to be

$$\eta_e^0 C_1 = \left( \eta_e^0 u_p - \eta_s u_p \frac{\theta_p^0}{\theta_s^0} \right) \theta_1 \Big|_{y=1} - \frac{L^2}{2} \theta_p^0 u_p. \quad (3.32)$$

We integrate (3.31) to find

$$\eta_e^0 \theta_p^0 v_1 \Big|_{y=1} + L \eta_s \frac{\theta_p^0}{\theta_s^0} u_p \theta_1 \Big|_{y=1} + L \eta_e^0 C_0 \int_0^1 \theta_1 dy - \frac{L^3}{6} \theta_p^0 u_p = L \eta_e^0 C_1, \quad (3.33)$$

so that, using (3.31) with (3.33), we get

$$\eta_e^0 \theta_p^0 \left( \frac{\partial v_1}{\partial y} - v_1 \Big|_{y=1} \right) = -L \eta_s \frac{\theta_p^0}{\theta_s^0} u_p \left( \frac{\partial}{\partial y} (y\theta_1) - \theta_1 \Big|_{y=1} \right) - L \eta_e^0 C_0 \theta_1 + \frac{L^3}{2} \theta_p^0 u_p \left( y^2 - \frac{1}{3} \right), \quad (3.34)$$

since  $\int_0^1 \theta_1 dy = 0$ .

Now the conservation equation (3.10) reduces to

$$\frac{\partial}{\partial \tau} (L\theta_p) + \xi \theta_p^0 \left( \frac{\partial v_1}{\partial y} - v_1 \Big|_{y=1} \right) = 0, \quad (3.35)$$

We set  $L\theta_p = L\theta_p^0 + \xi w$  with  $\int_0^1 w dy = 0$ . Using equations (3.34) and (3.35), we find that

$$\eta_e^0 \frac{\partial w}{\partial \tau} - \eta_s \frac{\theta_p^0}{\theta_s^0} u_p \left( \frac{\partial}{\partial y} (yw) - w \Big|_{y=1} \right) - \eta_e^0 C_0 w + \frac{L^3}{2} \theta_p^0 u_p \left( y^2 - \frac{1}{3} \right) = 0. \quad (3.36)$$

The solution of this equation can be found in terms of the polynomials,  $P_k(y) = y^k - \frac{1}{k+1}$ , as

$$w = \sum_{k=1}^{\infty} \beta_k P_k(y). \quad (3.37)$$



This is because the polynomials  $P_k(y)$  are eigenfunctions of the linear operator

$$\mathcal{L}w = \frac{\partial}{\partial y}(yw) - w \Big|_{y=1}, \quad (3.38)$$

i.e.

$$\mathcal{L}P_k = (k+1)P_k, \quad (3.39)$$

and being polynomials, they are obviously linearly independent. Substituting directly into (3.36) we find

$$\frac{d\beta_k}{d\tau} + \frac{1}{\eta_e^0} \left( -\eta_s \frac{\theta_p^0}{\theta_s^0} u_p (k+1) - \eta_e^0 C_0 \right) \beta_k + \frac{1}{\eta_e^0} \frac{L^2}{2} L \theta_p^0 u_p \delta_{2k} = 0. \quad (3.40)$$

If  $\theta_p$  is initially uniform, then  $\beta_k = 0$  at  $\tau = 0$  and subsequently  $\beta_k = 0$  for  $k \neq 2$  for all time. We are left with a single equation for  $\beta_2$ ,

$$\frac{d\beta_2}{d\tau} + \frac{1}{\eta_e^0} \left( -2\eta_s \frac{\theta_p^0}{\theta_s^0} u_p - \eta_e^0 u_p + \theta_p^0 \theta_s^0 f''(\theta_p^0) \right) \beta_2 + \frac{1}{\eta_e^0} \frac{L^2}{2} L \theta_p^0 u_p = 0. \quad (3.41)$$

Furthermore, from the definition of  $w$  and (3.33), it follows that

$$\eta_e^0 \theta_p^0 v_1 \Big|_{y=1} = \frac{2}{3} \left( \eta_e^0 u_p - 2\eta_s u_p \frac{\theta_p^0}{\theta_s^0} \right) \beta_2 - \frac{L^2}{3} L \theta_p^0 u_p, \quad (3.42)$$

so that, from (3.13),

$$\frac{dL}{d\tau} = u_p L + \frac{\xi u_p}{\eta_e^0 \theta_p^0} \left( \frac{2}{3} \left( \eta_e^0 - 2\eta_s \frac{\theta_p^0}{\theta_s^0} \right) \beta_2 - \frac{L^2}{3} L \theta_p^0 \right). \quad (3.43)$$

Using that  $L\theta_p^0 = K$  is a constant, we find that

$$\frac{d\theta_p^0}{d\tau} = -u_p \theta_p^0 - u_p \theta_p^0 \frac{\xi}{3\eta_e^0} \left( 2 \left( \eta_e^0 - 2\eta_s \frac{\theta_p^0}{\theta_s^0} \right) \frac{\beta_2}{K} - L^2 \right), \quad (3.44)$$

$$\frac{d\beta_2}{dt} = \frac{1}{\eta_e^0} \left( \left( \eta_e^0 + 2\eta_s \frac{\theta_p^0}{\theta_s^0} \right) u_p - \theta_p^0 \theta_s^0 f''(\theta_p^0) \right) \beta_2 - \frac{1}{\eta_e^0} \frac{L^2 K}{2} u_p. \quad (3.45)$$

Here we have a system of two differential equations that fully describe the expansion (or contraction) of the gel. The behavior of this system of equations is relatively easy to understand. The only steady solution of equation (3.44) has  $u_p \theta_p^0 = 0$ , which, since  $\eta_e^0 u_p = \theta_s^0 f'(\theta_p^0)$  (see (3.27)), implies that  $\theta_p^* \theta_s^* f'(\theta_p^*) = 0$  and  $\beta_2 = 0$ , as expected. Furthermore, if this steady solution has  $f'(\theta_p^*) = 0$ , then the solution is stable if  $f''(\theta_p^*)$  is positive, also as before.

The time constant is modified slightly. If  $f$  has an interior minimum, then the time constant  $\tau_p$  is

$$\tau_p = \frac{\eta_e^*}{\theta_p^* \theta_s^* f''(\theta_p^*)} \left( 1 + \frac{\xi L^2}{3\eta_e^*} + O\left(\frac{\xi L^2}{\eta_e^*}\right)^2 \right). \quad (3.46)$$

Thus, we see that the rate of swelling is size dependent when  $\xi$  is not zero.

**3.7. Linearized Analysis.** We can also determine the time constant for swelling using a linearized analysis of the governing equations. We assume that  $v_p$  and  $v_s$  are small, and that  $\theta_p = \theta_p^* + \delta\theta_p$ , where  $\theta_p^*$  is the steady state value of polymer volume fraction. The linearization of the force balance equation (3.11) is

$$\eta_e^* \frac{\partial^2 v_p}{\partial y^2} - \xi L^2 v_p - L \theta_s^* f''(\theta_p) \frac{\partial \delta\theta_p}{\partial y} = 0, \quad (3.47)$$

subject to boundary conditions

$$\eta_e^* \frac{\partial v_p}{\partial y} = L \theta_s^* f''(\theta_p^*) \delta \theta_p, \quad (3.48)$$

at  $y = 1$ , and  $v_p = 0$  at  $y = 0$ . The linearization of the conservation equation (3.10) is

$$\frac{\partial(\delta(L\theta_p))}{\partial \tau} = -\theta_p^* \left( \frac{\partial v_p}{\partial y} - v_p(1) \right), \quad (3.49)$$

but since  $\delta(L\theta) = \theta_p^* \delta L + L \delta \theta_p$  this reduces to

$$L \frac{\partial(\delta \theta_p)}{\partial \tau} = -\theta_p^* \frac{\partial v_p}{\partial y}. \quad (3.50)$$

We can express this system as a single partial differential equation by setting  $z = L \theta_s^* f''(\theta_p^*) \delta \theta_p - \eta_e^* \frac{\partial v_p}{\partial y}$ , in terms of which (3.47) becomes

$$\frac{\partial z}{\partial y} + \xi L^2 v_p = 0, \quad (3.51)$$

so that

$$\frac{\partial}{\partial \tau} \left( z - \frac{\eta_e^*}{\xi L^2} \frac{\partial^2 z}{\partial y^2} \right) = \frac{\theta_p^* \theta_s^* f''(\theta_p^*)}{\xi L^2} \frac{\partial^2 z}{\partial y^2}, \quad (3.52)$$

subject to boundary conditions  $z = 0$  at  $y = 1$  and  $\frac{\partial z}{\partial y} = 0$  at  $y = 0$ .

We can find solutions of this problem using appropriate eigenfunctions. That is, with

$$\delta \theta_p = a \cos(\omega y), \quad v_p(y) = b \sin(\omega y), \quad (3.53)$$

the force balance equation (3.47) is satisfied if

$$b = \frac{\omega}{\eta_e^* \omega^2 + \xi L^2} L \theta_s^* f''(\theta_p^*) a. \quad (3.54)$$

With these functions the linearized conservation equation (3.49) reduces to

$$\frac{da}{d\tau} = -\frac{\omega^2 \theta_p^* \theta_s^* f''(\theta_p^*)}{\eta_e^* \omega^2 + \xi L^2} a. \quad (3.55)$$

Finally, in order for the boundary conditions to be satisfied it must be that

$$\frac{\omega \xi L^2}{\eta_e^* \omega^2 + \xi L^2} \cos(\omega) = 0, \quad (3.56)$$

so that  $\omega_n = (2n - 1) \frac{\pi}{2}$  for  $n = 1, 2, \dots$ .

Associated with each of these eigenfunctions, there is a time constant for decay. The largest such time constant is the one associated with  $\omega_n = \frac{\pi}{2}$ , yielding

$$\tau_p = \frac{1}{\theta_p^* \theta_s^* f''(\theta_p^*)} \left( \eta_e^* + \frac{4\xi L^2}{\pi^2} \right). \quad (3.57)$$

We note, however, that in the limit  $\xi \rightarrow 0$ , all time constants approach  $\frac{\eta_e^*}{\theta_p^* \theta_s^* f''(\theta_p^*)}$ , so all eigenfunctions decay at about the same rate, and therefore the shape of the solution is not well described by a single eigenfunction. Thus, this characterization of the decay of the solution is not appropriate in the limit that  $\xi \rightarrow 0$ .

This answer also illustrates the limitations of the Tanaka-Fillmore theory that the kinetics of a swelling gel are governed by a diffusion equation. Instead, we find that the dynamics are governed by a diffusion equation in the limit  $\frac{\eta_e^*}{\xi L^2} \rightarrow 0$ , but differ significantly from a purely diffusion process in the limit  $\xi \rightarrow 0$ .

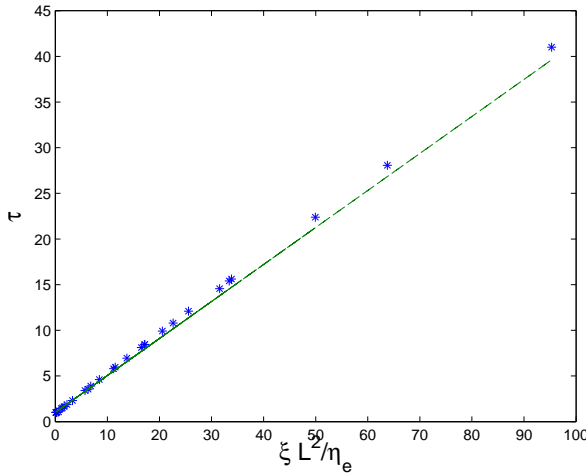


FIG. 4.1. The computed scaled time constant  $\frac{\tau_p \theta_p^* \theta_s^* f''(\theta_p^*)}{\eta_e^*}$ , shown as \*'s, compared to the line  $1 + \frac{4\xi L^2}{\eta_e^* \pi^2}$ , plotted as a function of  $\frac{\xi L^2}{\eta_e^*}$ .

**4. Some Examples.** To further illustrate how gels swell or deswell, we performed numerical simulations of the governing equations. We chose a free energy function of the form

$$f(\theta_p) = k_b T \left[ \frac{\theta_p}{N} \log(\theta_p) + (1 - \theta_p) \log(1 - \theta_p) \right] + \chi \theta_p (1 - \theta_p) + (\mu_p^0 - \mu_s^0) \theta_p + \mu_s^0, \quad (4.1)$$

where  $\chi$  is the Flory interaction energy parameter,  $\mu_p^0$  is the standard free energy for the polymer,  $\mu_s^0$  is the standard free energy of the solvent and  $N$  is the length of the polymer. Without loss of generality, we take  $\mu_s^0 = 0$ . In nondimensional units, we chose  $k_b T = 1$ ,  $\chi = -2$ , and  $N = 100$ . With these parameter values  $f$  has a unique minimum.

The numerical simulation of these equations was relatively straightforward. At each time step, we determined the velocity by solving the force balance equation (3.11) using finite differences on a uniform spatial grid. We then stepped the conservation equation (3.10) forward in time using first order upwinding. The boundary values of  $\theta_p$  were determined by directly integrating (3.10) at  $y = 0, 1$ .

**4.1. Swelling Gels.** To simulate a swelling gel we chose  $\mu_p^0 = 2.507$ . With this choice of  $\mu_p^0$ , the unique equilibrium is at  $\theta_p^* = 0.1$ . We then chose  $\theta_p = 0.5$  and  $L = 0.2$  at time  $t = 0$  so that the final size of the swelled gel is  $L = 1.0$ .

First, to verify the calculated time constant (3.57), we simulated expansion for a large number of different choices of viscosity and drag. In Fig. 4.1 we show the computed scaled time constant  $\frac{\tau \theta_p^* \theta_s^* f''(\theta_p^*)}{\eta_e^*}$ , shown as \*'s, compared to the line  $1 + \frac{4\xi L^2}{\eta_e^* \pi^2}$ . Clearly the computed solution is in very good agreement with the result from linearized analysis.

In spite of the good agreement shown in this figure, the expansion of a gel is not completely characterized by its time constant. To illustrate this fact, in Figs. 4.2, 4.3 and 4.4 are shown various features of swelling gels, all with exactly the same time constants. Fig. 4.2 shows the value of  $\theta_p$  at the interface; Fig. 4.3 shows the length of the gel as a function of time; and Fig. 4.4 shows the log of  $L^* - L$  as a function of time. From this last plot it is clear that all gels simulated here have the same time constant, since the asymptotic slope on a log scale is the same for all four curves. However, there is a noticeable difference in the way these gels expand before they approach the regime for which a linear analysis is appropriate. In particular, the expansion of gels with small drag (Cases 1 and 2) is noticeably slower than the expansion of gels with small viscosity (Cases 3 and 4).

The detailed profiles are shown in Figs. 4.5-4.8, and the parameter values are shown in Table 4.1. Here are shown plots of  $\theta_p$  plotted as a function of  $x$  at several times; in order to keep the difference between profiles relatively constant, the times are such that the change in  $\int_0^1 \theta_p(y) dy$  is held constant. The details

Case #	Fig.	$\eta_s$	$\eta_p$	$\xi$	$\frac{\xi L^2}{\eta_e^*}$
1	Fig. 4.5	0.0100	1.0199	0.2000	0.2176
2	Fig. 4.6	9.5047	0.0100	0.1000	0.1042
3	Fig. 4.7	0.0100	0.1000	2.2429	24.6469
4	Fig. 4.8	0.1000	0.0100	2.4205	127.3958

TABLE 4.1

Parameter values (viscosity and drag) for swelling gels.

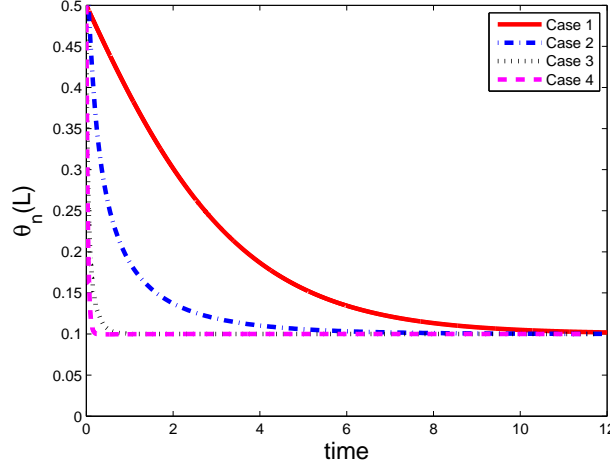


FIG. 4.2.  $\theta_p$  at the gel interface plotted as a function of time for four expanding gels. Parameter values are shown in Table 4.1.

of these are as follows: Figs. 4.5 and 4.6 have small drag and a large viscosity ( $\frac{\xi L^2}{\eta_e^*} \ll 1$  with large  $\eta_p$  in Fig. 4.5 and large  $\eta_s$  in Fig. 4.6), while in Fig. 4.7 and 4.8 the gels have small viscosity and large drag  $\frac{\xi L^2}{\eta_e^*} \gg 1$ . The spatial profile of  $\theta_p$  for the first two of these (Figs. 4.5 and 4.6) is relatively flat for all times, a consequence of small drag. The difference between the spatial profiles for these two is difficult to see. However, the difference in temporal behavior is evident in Figs. 4.2 and 4.4; with Case 1 (large  $\eta_p$ ), expansion is much slower than Case 2 (large  $\eta_s$ ). In contrast, the spatial profile of the second two of these is better described by a cosine function, also reflective of the fact that viscosity is small. For these cases, expansion occurs first at the edge of the gel and migrates into the interior. However, between these two there are also noticeable differences, coming from the different effects of polymer viscosity vs. solvent viscosity. That is, solvent viscosity and polymer viscosity are not interchangeable. Of course, this is easy to understand since  $\eta_e$  is not symmetric with respect to solvent and polymer viscosity. It is this difference that leads to noticeable differences in the speed of nonlinear expansion of the gel.

**4.2. Deswelling Gels.** To examine deswelling gels, we set  $\mu_p^0 = 0.303$  for which  $\theta_p^* = 0.5$ . We chose  $\theta_p = 0.1$  and  $L = 5$  at time  $t = 0$  so that the final length is once again  $L^* = 1$ . In Figs. 4.9, 4.10 and 4.11 are shown various features of the deswelling gels, all with the same time constant. Fig. 4.9 shows the value of  $\theta_p$  at the interface; Fig. 4.10 shows the length of the gel as a function of time; and Fig. 4.11 shows the log of  $L - L^*$  as a function of time. The curves in Fig. 4.11 show that all of the gels have the same time constant. As in the case of swelling, the four gels contract differently before they approach the regime where the time constant is relevant. However, there is a noticeable difference in the way these gels contract before they approach the regime for which a linear analysis is appropriate. In particular, the contraction of gels with small drag is noticeably faster than the contraction of gels with small viscosity.

The detailed profiles are shown in Figs. 4.12-4.15. Here are shown plots of  $\theta_p$  plotted as a function of  $x$  at several times with times chosen so that the change in  $\int_0^1 \theta_p(y) dy$  between times is constant. The parameter values for these gels are given in Table 4.2. Figs. 4.12 and 4.13 have small drag and one large

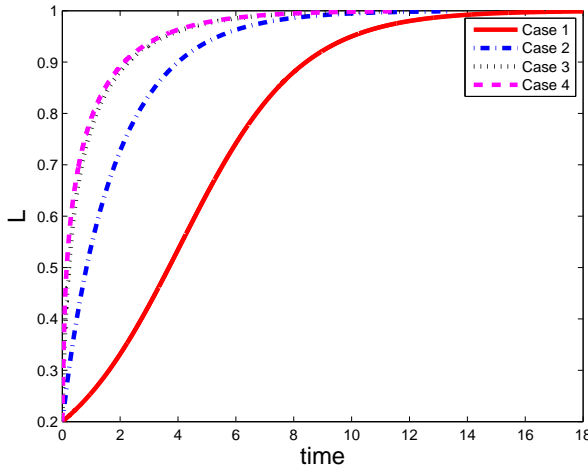


FIG. 4.3. The length of the gel,  $L(t)$  plotted as a function of time, for four different expanding gels with the same time constant. Parameter values are shown in Table 4.1.

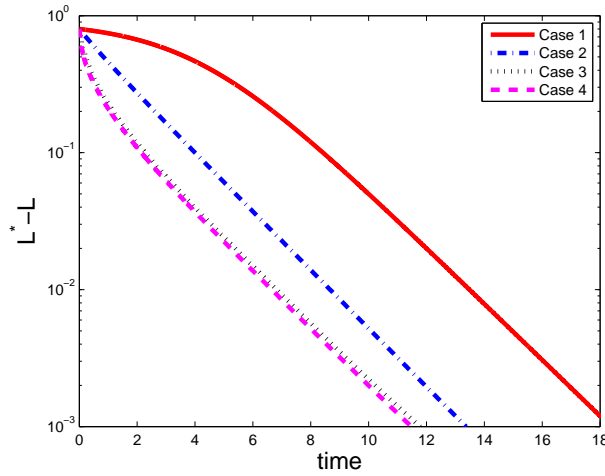


FIG. 4.4.  $\log(L^* - L(t))$  plotted as a function of time for four different gels with the same time constant. Parameter values are shown in Table 4.1.

viscosity ( $\frac{\xi L^2}{\eta_c} \ll 1$ , large  $\eta_p$  in Fig. 4.5 and large  $\eta_s$  in Fig. 4.6), while in Fig. 4.14 and 4.15 the gels have small viscosity and large drag  $\frac{\xi L^2}{\eta_c} \gg 1$ .

The first observation is that deswelling occurs from the outside in. That is, the outside of the gel compresses first and fastest and the interior of the gel compresses last and slowest. When drag is small, the profile remains relatively flat, while if the viscosity is small,  $\theta_p$  at the interface approaches equilibrium quite fast, giving rise to a significantly nonuniform profile for  $\theta_p$ . Again, there is very little difference between the profiles in Figs. 4.12 and 4.13. The differences between these two can be seen in Figs. 4.2 and 4.11. In contrast to the case of swelling, deswelling is slower for a gel with large drag than for a gel with large viscosity, even though the time constants are identical. In fact, as seen in Fig. 4.11, the deswelling kinetics of a gel with large drag is not well characterized by the linearized approximation.

**5. Discussion.** In this paper we have provided a fully nonlinear theory for the expansion and contraction of gels, with no assumptions on the relative volume fraction of polymer and solvent (i.e., the polymer is not assumed to be dilute). We show how the kinetics of gel expansion are related to the free energy

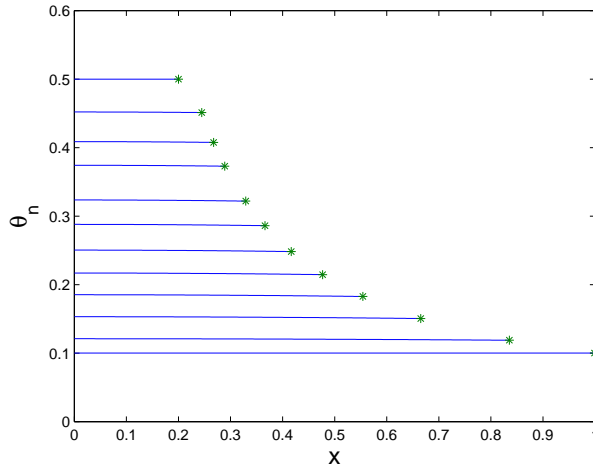


FIG. 4.5. Profile for  $\theta_p$  at selected times for a swelling gel with small drag. Parameter values are listed in Table 4.1, Case 1.

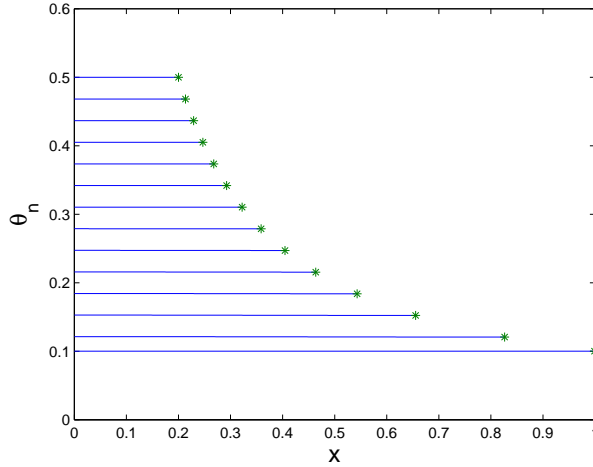


FIG. 4.6. Profile for  $\theta_p$  at selected times for a swelling gel with small drag. Parameter values are listed in Table 4.1, Case 2.

as well as the rheological properties of the gel, namely polymer viscosity, solvent viscosity and drag. Our results extend the classical result of Tanaka and Fillmore [25], showing that the time constant is a linear function of  $L^2$ . However, we find that the viscosity of the gel and the drag of the gel have different effects, leading to an additional term (a nonzero intercept) for this linear function. This theory predicts that a more careful analysis of experimental data provides the opportunity to determine the viscosity and drag as separate rheological parameters.

The model presented here is different from previous models in at least two regards: First, we include in the force balance equations forces from the solvent chemical potential as well as forces from the polymer chemical potential, thereby satisfying Newton's third law. This inclusion eliminates the need to assume that the polymer network is dilute, since the force of the polymer on the solvent is not neglected. Second, chemical potential is determined from the total free energy; previous formulations of this problem used the mixing free energy rather than the total free energy. Using the mixing free energy, the polymer standard free energy is neglected with the consequence that both the equilibrium states and the diffusivity are modified. Notice that in our examples above, the equilibrium state of the gel was changed simply by changing the value of the standard free energy  $\mu_p^0$ . Consequences of this are described in more detail in other publications [15].

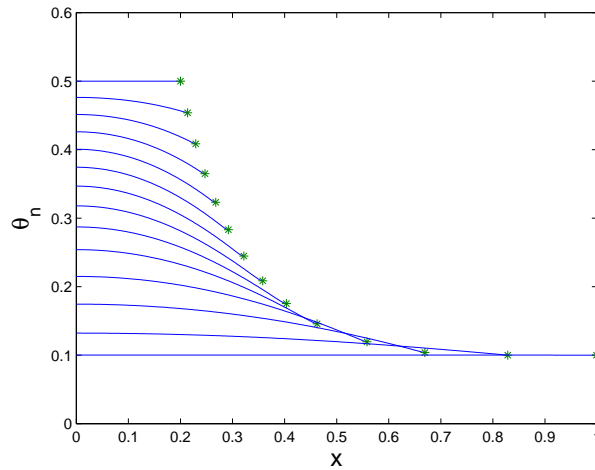


FIG. 4.7. Profile for  $\theta_p$  at selected times for a swelling gel with small viscosity. Parameter values are listed in Table 4.1, Case 3.

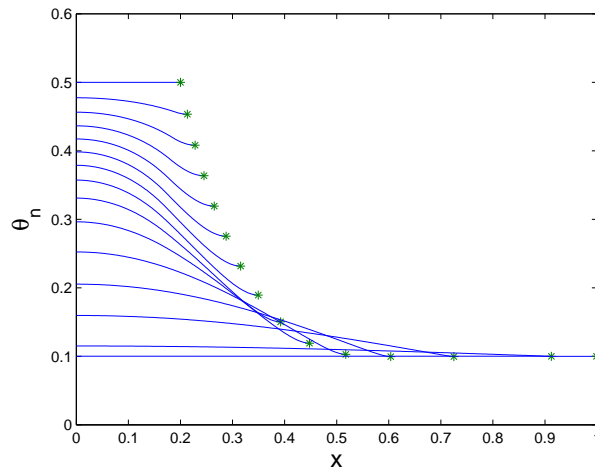


FIG. 4.8. Profile for  $\theta_p$  at selected times for a swelling gel with small viscosity. Parameter values are listed in Table 4.1, Case 4.

#### REFERENCES

- [1] G. K. Batchelor. *An Introduction to Fluid Dynamics*. Cambridge University Press, Cambridge, 1967.
- [2] N. Cogan and J. P. Keener. The role of the biofilm matrix in structural development. *Mathematical Medicine and Biology*, 21, 2004.
- [3] M. Doi. *Introduction to Polymer Dynamics*. Oxford University Press, Oxford, England, 1996.
- [4] M. Doi and S. F. Edwards. *Theory of Polymer Dynamics*. Clarendon Press, Oxford, England, 1986.
- [5] C. J. Durning and K. N. Morman. Nonlinear swelling of polymer gels. *J Chem Phys*, 98:4275–4293, 1993.
- [6] P. J. Flory. *Principles of Polymer Chemistry*. Cornell University Press, Ithaca, NY, 1953.
- [7] P. J. Flory. Statistical thermodynamics of random networks. *Proc. R. Soc. Lond. A.*, 351:351–380, 1976.
- [8] P. J. Flory and J. Rehner Jr. Statistical mechanics of crosslinked polymer networks I. rubberlike elasticity. *Journal of Chemical Physics*, 11:512, 1943.
- [9] P. J. Flory and J. Rehner Jr. Statistical mechanics of crosslinked polymer networks II. swelling. *Journal of Chemical Physics*, 11(11):521, 1943.
- [10] A. Girgidov. Energy dissipation in the motion of an incompressible fluid. *Doklady Physics*, 54:306–308, 2009.
- [11] W. Y. Gu, W. M. Lai, and V.C. Mow. A mixture theory for charged-hydrated soft tissues containing multi-electrolytes: Passive transport and swelling behaviors. *Trans ASME J. Biomech. Eng.*, 120:169–180, 1998.
- [12] X. He and M. Dembo. On the mechanics of the first cleavage division of the sea urchin egg. *Exp. Cell Res.*, 233:252–273,

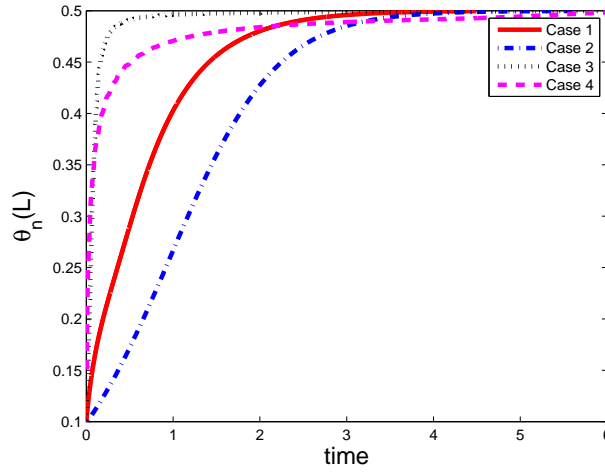


FIG. 4.9.  $\theta_p(y = 1)$  plotted as a function of time for four different deswelling gels with the same time constant. Parameter values are shown in Table 4.2.

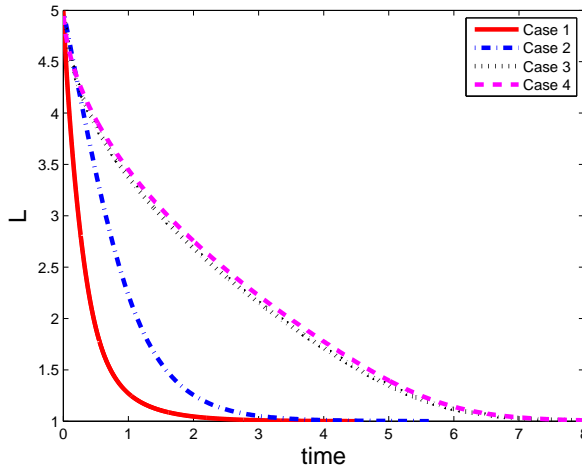


FIG. 4.10. The length of a deswelling gel  $L(t)$  plotted as a function of time for four different deswelling gels with the same time constant. Parameter values are shown in Table 4.2.

1997.

- [13] J. S. Hou, M. H. Holmes, W. M. Lai, and V. C. Mow. Boundary conditions at the cartilage-synovial fluid interface for joint lubrication and theoretical verifications. *J Biomech Eng*, 111(1):78–87, 1989.
- [14] A. Katchalsky and I. Michaeli. Polyelectrolyte gels in salt solutions. *J Polym Sci*, 15:69–86, 1955.
- [15] J. P. Keener, S. Sircar, and A. L. Fogelson. The influence of the standard free energy on swelling kinetics of gels. *Phys. Rev. E*, to appear, 2010.
- [16] W. M. Lai, J. S. Hou, and V. C. Mow. A triphasic theory for the swelling and deformation behaviors of articular cartilage. *J. Biomech. Eng.*, 113(245-258), 1991.
- [17] Y. Lanir. Plausibility of structural constitutive equations for swelling tissues-implications of the c-n and s-e conditions. *Trans ASME J. Biomech. Eng.*, 118(10-16), 1996.
- [18] V. Lyul'ka. On the principle of minimum kinetic energy dissipation in the nonlinear dynamics of viscous fluid. *Technical Physics*, 46:1501–1503, 2001.
- [19] J. Maskawa, T. Takeuchi, K. Maki, K. Tsuijii, and T. Tanaka. Theory and numerical calculation of pattern formation in shrinking gels. *J. Chem Phys*, 110:10993–10999, 1999.
- [20] S. T. Milner. Hydrodynamics of semidilute polymer solutions. *Phys. Rev. Lett.*, 66(11):1477, 1991.
- [21] S. T. Milner. Dynamical theory of concentration fluctuations in polymer-solutions under shear. *Physical Review E*, 48(5):3674–3691, 1993.
- [22] A. Onuki. Theory of pattern formation in gels: surface folding in highly compressible elastic bodies. *Phys. Rev. A*,



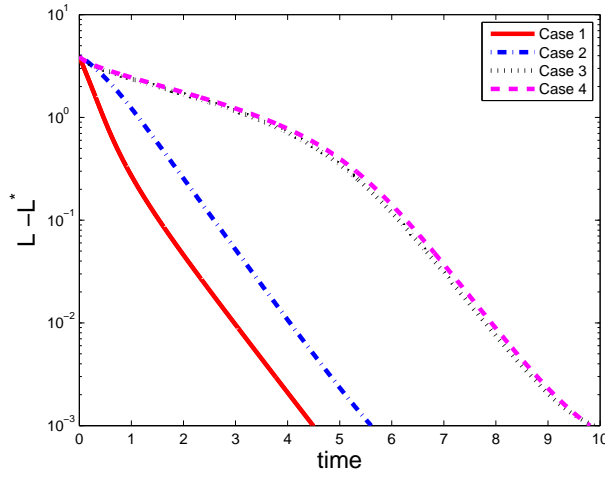


FIG. 4.11.  $\log_{10}(L(t) - L^*)$  plotted as a function of time for four different deswelling gels with the same time constant. Parameter values are shown in Table 4.2.

Case#	Fig.	$\eta_s$	$\eta_p$	$\xi$	$\frac{\xi L^2}{\eta_s^2}$
1	Fig. 4.12	0.0100	1.8279	0.2000	0.2176
2	Fig. 4.13	1.9089	0.0100	0.1000	0.1042
3	Fig. 4.14	0.0100	0.1000	2.3317	42.3944
4	Fig. 4.15	0.1000	0.0100	2.3317	42.3944

TABLE 4.2  
Parameter values for deswelling gels.

- 39:5932–5948, 1989.
- [23] G. F. Oster and G. M. Odell. The mechanochemistry of cytogels. *Physica D*, 12:333–350, 1984.
- [24] K. Sekimoto, N. Suematsu, and K. Kawasaki. Spongelike domain structure in a two-dimensional model gel undergoing volume-phase transition. *Phys. Rev. A*, 39:4912–4914, 1989.
- [25] T. Tanaka and D. J. Fillmore. Kinetics of swelling in gels. *J Chem Phys*, 70:1214–1218, 1979.
- [26] T. Tanaka, D. Filmore, S. T. Sun, I. Nishio, G. Swislow, and A. Saha. Phase transition in ionic gels. *Phys. Rev. Lett.*, 45(20):1636, 1980.
- [27] C. Wang, Y. Li, and Z. Hu. Swelling kinetics of polymer gels. *Macromolecules*, 30:4727–4732, 1997.
- [28] C. Wolgemuth, E. Hoiczky, D. Kaiser, and G. Oster. How myxobacteria glide. *Current Biology*, 12(5):369–377, March 2002.
- [29] C. Wolgemuth, A. Mogilner, and G. Oster. The hydration dynamics of polyelectrolyte gels with applications to cell motility and drug delivery. *Eur. Biophys. J.*, 33:146–158, 2004.
- [30] C. W. Wolgemuth, E. Hoiczky, and G. Oster. How gliding bacteria glide. *Biophysical Journal*, 82(1):1956, January 2002.
- [31] T. Yamaue, T. Taniguchi, and M. Doi. Shrinking process of gels by stress-diffusion coupled dynamics. *Prog. Theor. Phys. Supp.*, 138:416–417, 2000.
- [32] T. Zhang, N. Cogan, and Q. Wang. Phase field models for biofilms. I. theory and one-dimensional simulations. *SIAM J. Appl. Math.*, 69(3):641–669, 2008.
- [33] T. Zhang, N. Cogan, and Q. Wang. Phase field models for biofilms. II. 2-D numerical simulations of biofilm-flow interaction. *Comm. Comp. Phys.*, 4(1):72–101, 2008.

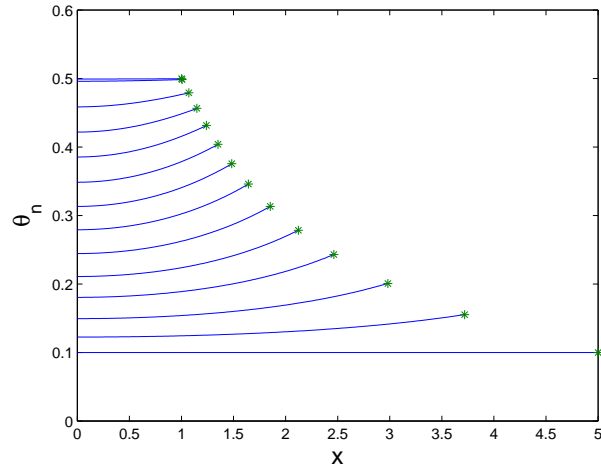


FIG. 4.12. Profile for  $\theta_p$  at selected times for a deswelling gel with small drag. Parameter values are listed in Table 4.2, Case 1.

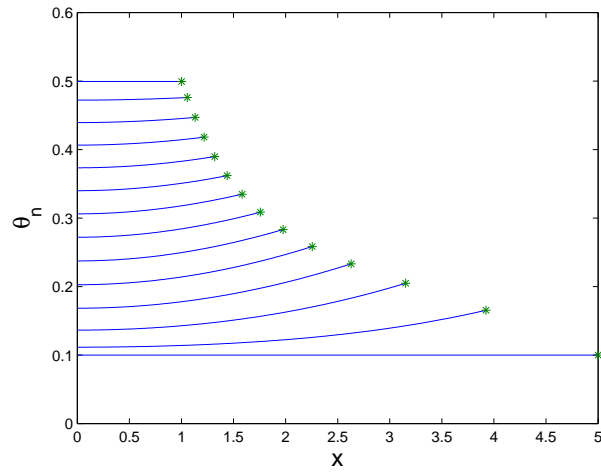


FIG. 4.13. Profile for  $\theta_p$  at selected times for a deswelling gel with small drag. Parameter values are listed in Table 4.2, Case 2.

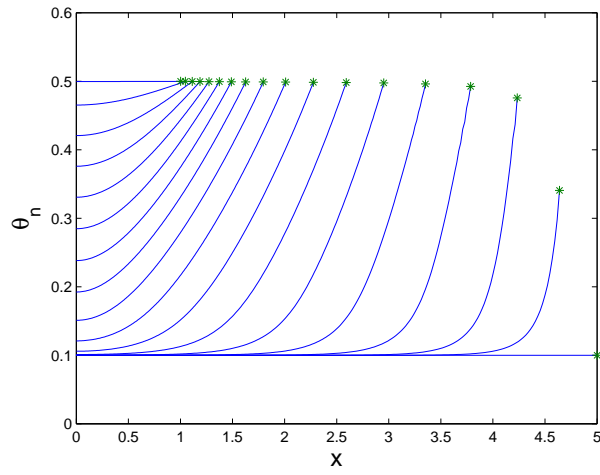


FIG. 4.14. Profile for  $\theta_p$  at selected times for a deswelling gel with small viscosity. Parameter values are listed in Table 4.2, Case 3.

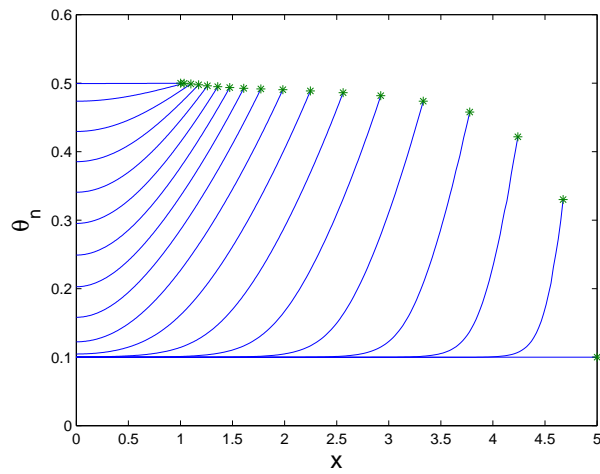


FIG. 4.15. Profile for  $\theta_p$  at selected times for a deswelling gel with small viscosity. Parameter values are listed in Table 4.2, Case 4.