Electronic Supplementary Information (ESI)

**Swelling kinetics of polymer gels: comparison of linear and nonlinear Theories**

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**Appendix A: Linear elastic properties of gel**

To determine the linear elastic properties of a swollen gel based on the nonlinear theory, we assume that the gel is in chemical equilibrium and thus the chemical potential remains a constant everywhere in the gel during deformation. Take the initial state of the gel to be stress free and isotropically swollen with a swelling ratio  in all directions, relative to the dry state. The chemical potential in the gel is thus fixed by the swelling ratio as given in Eq. (3.1). Now consider three simple loading conditions imposed on the swollen gel: uniaxial stress, hydrostatic pressure, and simple shear.

Under a uniaxial stress, the only non-zero component of the nominal stress is

  (A1)

where  is the true stress in the 1-direction and  is the stretch in the lateral direction (relative to the dry state).

By the nonlinear constitutive relation in (2.7), we obtain that

  (A2)

  (A3)

where

  (A4)

By setting , we obtain the lateral stretch () as a function of the axial stretch (), namely

  (A5)

 For a small deformation from the initial state, we have

  and  (A6)

where ε1 and ε2 are the linear strain components in the axial and lateral directions, respectively. Assuming , we linearize Eq. (A5) and obtain

  (A7)

Poisson’s ratio of the swollen gel is then defined as

  (A8)

which is used in (3.7).

 Combining (A1) and (A2), we obtain the axial stress as a function of the axial stretch:

  (A9)

Linearizing (A9) leads to

  (A10)

Thus, Young’s modulus of the swollen gel is

  (A11)

 Therefore, by considering the equilibrium deformation of the swollen gel under a uniaxial stress, we determine Young’s modulus and Poisson’s ratio as the linear elastic properties under the condition of small deformation () based on the nonlinear theory.

Next consider the swollen hydrogel under a hydrostatic pressure *p*. In this case, the swelling ratio of the gel remains isotropic, i.e., . Correspondingly, the nominal stresses are

  (A12)

Inserting (A12) into (A2), we obtain the swelling ratio as a function of the pressure:

  (A13)

By (A13), the swelling ratio () decreases as the external pressure increases. In other words, applying external pressure directly onto the gel, not through the solvent, can squeeze out solvent molecules. On the other hand, applying pressure through the solvent would change the chemical potential in the gel and the external solvent simultaneously, which would not change the volume of the gel.

By linearizing (A13), a bulk modulus of the swollen gel can be defined as

  (A14)

With Young’s modulus in (A11) and Poisson’s ratio in (A8), it can be confirmed that the bulk modulus, , consistent with the linear elasticity theory.

For simple shear, we assume a deformation gradient

  (A15)

where  is the shear strain imposed onto the initial state of the gel. By the constitutive relation in (2.7), the only non-zero component of the nominal stress is

  (A16)

The true shear stress is obtained as

  (A17)

Thus the shear modulus of the swollen gel is

  (A18)

which is used in Eq. (3.7). Again, it can be confirmed that the Young’s modulus in (A11), Poisson’s ratio in (A8), and the shear modulus in (A18) satisfy the relationship for isotropic linear elasticity: .

It is notable that the nonlinear theory predicts a linear relationship between the shear strain and shear stress for the case of simple shear while the stress-strain behavior under uniaxial stress and hydrostatic pressure is nonlinear in general.

**Appendix B: Solution procedures for constrained and free swelling**

**B.1 Constrained swelling by the nonlinear theory**

For constrained swelling of a thin layer, the stretch in the thickness direction is a function of time and position, , whereas . By the nonlinear theory, the nominal stresses in the gel are obtained from Eq. (2.7):

  (B1)

  (B2)

The mechanical equilibrium equation in (2.8) requires that

  (B3)

With the traction-free boundary condition at the upper surface, i.e., , we have  everywhere in the gel and hence by (B2)

  (B4)

Next, inserting (B4) into (2.6), the chemical potential in the gel is obtained:

  (B5)

The nominal mobility as defined in (2.11) is specialized for this case as:

  (B6)

  (B7)

and . Thus, by (2.10), we have  and

  (B8)

where

  (B9)

Finally, the diffusion equation (2.12) becomes

  (B10)

The nonlinear diffusion equation in (B10) is solved numerically by a finite difference method. After normalizing the time and spatial coordinate as $\overbar{t}=\frac{tD}{H^{2}}$ and $\overbar{X}=\frac{X\_{2}}{H}$, the diffusion equation takes a dimensionless form

 (B11)

By the finite difference method, we integrate (B11) at each node with $\overbar{X}\_{i}=(i-1)∆X$ for *i* = 2 to *n* and $∆X=1/n$:

$λ\_{2}\left(\overbar{X}\_{i},\overbar{t}+∆t\right)=λ\_{2}\left(\overbar{X}\_{i},\overbar{t}\right)-\frac{∆t}{∆X}\left[J\left(\overbar{X}\_{i}+\frac{∆X}{2},\overbar{t}\right)-J\left(\overbar{X}\_{i}-\frac{∆X}{2},\overbar{t}\right)\right]$ (B12)

where

$J\left(\overbar{X}\_{i}+\frac{∆X}{2},\overbar{t}\right)=-ξ\left(\overbar{X}\_{i}+\frac{∆X}{2},\overbar{t}\right)\frac{λ\_{2}\left(\overbar{X}\_{i+1},\overbar{t}\right)-λ\_{2}\left(\overbar{X}\_{i},\overbar{t}\right)}{λ\_{0}^{2}∆X}$ (B13)

and $ξ\left(\overbar{X}\_{i}+\frac{∆X}{2},\overbar{t}\right)$ is calculated using the swelling ratio at the midpoint by linear interpolation, i.e, $λ\_{2}\left(\overbar{X}\_{i}+\frac{∆X}{2},\overbar{t}\right)=\frac{λ\_{2}\left(\overbar{X}\_{i+1},\overbar{t}\right)+λ\_{2}\left(\overbar{X}\_{i},\overbar{t}\right)}{2}$.

The swelling ratio at the upper surface, $λ\_{2}\left(\overbar{X}\_{n+1},\overbar{t}\right)=λ\_{\infty }^{c}$, is fixed by the local equilibrium condition. At the lower surface (*X* = 0), the flux is zero and the swelling ratio is integrated as

$λ\_{2}\left(0,\overbar{t}+∆t\right)=λ\_{2}\left(0,\overbar{t}\right)-\frac{2∆t}{∆X}J\left(\frac{∆X}{2},\overbar{t}\right)$ (B14)

For the first step, $λ\_{2}\left(\overbar{X}\_{i},0\right)=λ\_{0}$, except at the upper surface. The numerical method is conditionally stable that requires a relatively small time step $∆t$. In our calculations for Fig. 2 and Fig. 3, we have used $∆X=0.02$ and $∆t=0.001$.

**B.2 Free swelling by the nonlinear theory**

For free swelling, solvent molecules enter the gel from both sides, and the gel swells in all directions. By symmetry, the layer remains flat, with  and . By the nonlinear theory the nominal stresses are

  (B15)

  (B16)

The mechanical equilibrium equation, along with the boundary condition, requires that  everywhere in the gel and thus

 . (B17)

By inserting (B17) into (2.6), the chemical potential in the gel is obtained:

  (B18)

The nominal mobility for this case is

 , (B19)

and the flux is

 . (B20)

where

 . (B21)

The nonlinear diffusion equation (2.12) then becomes

  (B22)

Furthermore, with no constraint in the in-plane directions, the in-plane stress must be self-balanced, namely

  (B23)

Inserting (B17) into (B23), we obtain that

 . (B24)

The two nonlinear equations (B22) and (B24) are solved simultaneously using a finite difference method. After normalization ($\overbar{t}=\frac{tD}{H^{2}}$ and $\overbar{X}=\frac{X\_{2}}{H}$), Eq. (B22) becomes

$λ\_{1}^{2}\frac{∂λ\_{2}}{∂\overbar{t}}+2λ\_{1}λ\_{2}\frac{dλ\_{1}}{d\overbar{t}}=\frac{∂}{∂\overbar{X}}[\overbar{ξ}(λ\_{1},λ\_{2})\frac{∂λ\_{2}}{∂\overbar{X}}]$ (B25)

We integrate (B25) at each node with $\overbar{X}\_{i}=(i-1)∆X$ for *i* = 2 to *n* and $∆X=1/n$:

$\left(λ\_{1}\right)^{2}\frac{\left(Δλ\_{2}\right)\_{i}}{∆t}+2λ\_{1}\left(λ\_{2}\right)\_{i}\frac{Δλ\_{1}}{∆t}=\frac{J\left(X\_{i}+\frac{∆X}{2}\right)-J\left(X\_{i}-\frac{∆X}{2}\right)}{∆X}$ (B26)

where

$J\left(X\_{i}+\frac{∆X}{2}\right)=\overbar{ξ}\left(λ\_{1},\frac{\left(λ\_{2}\right)\_{i}+\left(λ\_{2}\right)\_{i+1}}{2}\right)\frac{\left(λ\_{2}\right)\_{i+1}-\left(λ\_{2}\right)\_{i}}{∆X}$ (B27)

 The swelling ratio at the two end nodes (*i* = 1 and *n*+1) must satisfy the local equilibrium condition in (4.15), which may be written as $f\left(λ\_{1},λ\_{2}\right)=0$. Take the derivative of (4.15) with respect to $λ\_{1}$ and $λ\_{2}$, we obtain

$g\_{1}\left(λ\_{1},λ\_{2}\right)Δλ\_{1}+g\_{2}\left(λ\_{1},λ\_{2}\right)Δλ\_{2}=0$ (B28)

where $g\_{1}=∂f/∂λ\_{1}$ and $g\_{2}=∂f/∂λ\_{2}$.

 Discretization of (B24) leads to

  (B29)

The incremental form of (B29) is

  (B30)

 The discretized equations in (B26), (B28), and (B30) form a complete linear system that can be written in a matrix form as

 (B31)

where , **M** is a n+2 by n+2 matrix, and **P** is a vector of n+2 components. Thus, solving (B31) we obtain the increments for the swelling ratios, with which we update the swelling ratio for the next time step.

 For the first time step (*t* = 0+), the swelling ratios are obtained by solving the nonlinear equation (4.15) along with the conditions that $\left(λ\_{2}\right)\_{i}=λ\_{0}^{3}/λ\_{1}^{2}$ for *i* = 2 to *n* and $\left(λ\_{2}\right)\_{1,n+1}^{2}=nλ\_{1}^{2}-(n-1)λ\_{0}^{6}/λ\_{1}^{4}$. Again, the numerical method is conditionally stable. In our calculation for Fig. 4, we have used $∆X=0.02$ and $∆t=0.0025$.

**B.3 Free swelling by the linear poroelasticity theory**

A numerical method is used to solve Eqs. (4.16)-(4.18) by the linear poroelasticity theory for free swelling. For convenience, we normalize the chemical potential as $μ/GΩ$, the displacement as $u/h\_{0}$, and the time as $tD^{\*}/h\_{0}^{2}$. The normalized space domain is $z=x\_{2}/h\_{0}\in \left[0,1\right]$. The boundary conditions are: $μ\left(0,t\right)=0$, $μ\left(1,t\right)=0$, and $u\left(0,t\right)=0$. The initial conditions are: $μ\left(z,0\right)=μ\_{0}$ and $u\left(z,0\right)=0$. With a spatial discretization, $z\_{i}=(i-1)∆z$ for *i* = 1 to *n*+1 and $∆z=1/n$, we denote the nodal displacement and the chemical potential as: $u\_{i}(t)=u(z\_{i},t)$ and $μ\_{i}(t)=μ(z\_{i},t)$. The out-of-plane strain is then obtained at the midpoint as

 (B32)

By Eq. (4.18), the in-plane strain is obtained as

 (B33)

Next, Eq. (4.17) is discretized and written in a matrix form as

 (B34)

where **I** is the identity matrix (*n* by *n*), **U** is the unit matrix (*n* by *n*), and **V** is a *n* by *n*+1 matrix to obtain the chemical potential at the midpoints by linear interpolation as $μ\_{i+1/2}=(μ\_{ i}+μ\_{ i+1})/2$. Given the distribution of the chemical potential, the strain $\left\{\left(ε\_{22}\right)\_{i}, i=1-n\right\}$ can be obtained from (B34), and the in-plane strain $ε\_{11}$ can be obtained from (B33) at the same time step.

To integrate over time, Eq. (4.16) is discretized at each node (except for the two end nodes, where the chemical potential is fixed by the boundary condition) as

 (B35)

Moreover, taking time derivative of (B33) and (B34), we obtain that

 (B36)

 (B37)

The three rate equations, (B35)-(B37), can be solved simultaneously to find $\dot{μ}\_{i}$ (*i* = 2 to *n*), $\left(\dot{ε}\_{22}\right)\_{i}$ (*i* = 1 to *n*), and $\dot{ε}\_{11}$.

Using the forward finite difference scheme in time we update the values at time $t+Δt$ as

$μ\_{i}\left(t+∆t\right)=μ\_{i}\left(t\right)+\dot{μ}\_{i}Δt$ (B38)

$\left(ε\_{22}\right)\_{i}\left(t+∆t\right)=\left(ε\_{22}\right)\_{i}\left(t\right)+\left(\dot{ε}\_{22}\right)\_{i}Δt$ (B39)

$ε\_{11}\left(t+∆t\right)=ε\_{11}\left(t\right)+\dot{ε}\_{11}Δt$ (B40)

The procedure repeats itself to evolve the fields of chemical potential and the strain. The method is conditionally stable and requires a relatively small time step $Δt$. For the simulation in Fig. 9, we have used $Δt=0.0001$ and $Δz=0.02$.

Alternatively, by using the backward time difference, the method is more stable and allows using much larger time steps for faster calculations. Briefly, the rate equations can be written in a matrix form

 (B41)

where **u** represents a vector including all the variables, $μ\_{i}$ (*i* = 2 to *n*), $\left(ε\_{22}\right)\_{i}$ (*i* = 1 to *n*), and $ε\_{11}$. The two matrices **M** and **P** are independent of time. By backward difference, we obtain that

 (B42)

The vector can then be updated as

 (B43)