Supplementary information for

A theory of constrained swelling of a pH-sensitive hydrogel

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Part A: Coupled nonlinear algebraic equations

The nonlinear algebra equations (3.13)-(3.15) can be solved to express the concentrations in the gel, c_{H^+}, c_+ and c_-, in terms of the concentrations in the external solution, $\bar{c}_{\mathrm{H}^+}$, $\bar{c}_+$ and $\bar{c}_-$, and the swelling ratio $\det\mathbf{F}$. A combination of the three equations gives a cubic equation for $\upsilon c_{\mathrm{H}^+}$, namely,

$$\left(1+\frac{\upsilon\bar{c}_+}{\upsilon\bar{c}_{\mathrm{H}^+}}\right)\left(\upsilon c_{\mathrm{H}^+}\right)^3+N_A K_a\upsilon\left(1+\frac{\upsilon\bar{c}_+}{\upsilon\bar{c}_{\mathrm{H}^+}}\right)\left(\upsilon c_{\mathrm{H}^+}\right)^2-\left(\frac{N_A K_a\upsilon f}{\det\mathbf{F}}+\upsilon\bar{c}_{\mathrm{H}^+}\upsilon\bar{c}_-\right)\left(\upsilon c_{\mathrm{H}^+}\right)-N_A K_a\upsilon\upsilon\bar{c}_{\mathrm{H}^+}\upsilon\bar{c}_-=0. \tag{A.1}$$

The solution to this cubic equation is

$$\upsilon c_{\mathrm{H}^+}=\sqrt[3]{-\frac{q}{2}+\sqrt{\left(\frac{q}{2}\right)^2+\left(\frac{p}{3}\right)^3}}+\sqrt[3]{-\frac{q}{2}-\sqrt{\left(\frac{q}{2}\right)^2+\left(\frac{p}{3}\right)^3}}-\frac{N_A K_a\upsilon}{3}, \tag{A.2}$$

where

$$p=-\frac{\dfrac{N_A K_a\upsilon f}{\det\mathbf{F}}+\upsilon\bar{c}_{\mathrm{H}^+}\upsilon\bar{c}_-}{1+\dfrac{\upsilon\bar{c}_+}{\upsilon\bar{c}_{\mathrm{H}^+}}}-\frac{\left(N_A K_a\upsilon\right)^2}{3}, \tag{A.3}$$

$$q=-\frac{N_A K_a\upsilon\upsilon\bar{c}_{\mathrm{H}^+}\upsilon\bar{c}_-}{1+\dfrac{\upsilon\bar{c}_+}{\upsilon\bar{c}_{\mathrm{H}^+}}}+\frac{\left(N_A K_a\upsilon\right)\left(\dfrac{N_A K_a\upsilon f}{\det\mathbf{F}}+\upsilon\bar{c}_{\mathrm{H}^+}\upsilon\bar{c}_-\right)}{3\left(1+\dfrac{\upsilon\bar{c}_+}{\upsilon\bar{c}_{\mathrm{H}^+}}\right)}+\frac{2\left(N_A K_a\upsilon\right)^3}{27}. \tag{A.4}$$

Once c_{H^+} is solved, c_+ and c_- are solved from (3.13) and (3.14).

Recall that $\bar{c}_-=\bar{c}_{\mathrm{H}^+}+\bar{c}_+$ due to electroneutrality in the external solution, and that $C_\alpha=c_\alpha\det\mathbf{F}$ in the gel. Consequently, $\hat{W}$ defined in (5.1) can be expressed as a function of the following independent variables:

$$\hat{W}=\hat{W}\left(\mathbf{F},\bar{c}_{\mathrm{H}^+},\bar{c}_+\right). \tag{A.5}$$

In writing the user-supplied subroutine for ABAQUS, we also need partial derivatives of the function $\hat{W}\left(\mathbf{F},\bar{c}_{\mathrm{H}^+},\bar{c}_{+}\right)$. These lengthy expressions can be found in the subroutine and are not given here.

Part B: A gel of spherical symmetry

Boundary-value problems of spherical symmetry have been solved for neutral gels. [1,2] We now list the equations for a pH-sensitive gel. We name a small element of the network after the radius of the element, *R*, when the gel is in a state of reference. The same element of the network moves to a place of radius *r* when the gel is in the current state. The state of deformation of the gel is fully specified by the function $r(R)$. The stretch in each of the circumferential directions is

$$\lambda_\theta = r/R\,. \tag{B.1}$$

The stretch in the radial direction is

$$\lambda_r = dr/dR\,. \tag{B.2}$$

Let $s_\theta(R)$ be the nominal stress in each of the circumferential directions, and $s_r(R)$ be the nominal stress in the radial direction. Mechanical equilibrium requires that

$$\frac{ds_r}{dR}+2\frac{s_r-s_\theta}{R}=0\,. \tag{B.3}$$

Recall that the nominal stresses relate to the true stresses by $s_\theta=\sigma_\theta\lambda_r\lambda_\theta$ and $s_r=\sigma_r\lambda_\theta^2$. The stress-stretch relation (3.10) becomes that

$$s_\theta = NkT\left(\lambda_\theta-\lambda_\theta^{-1}\right)-\lambda_r\lambda_\theta\left(\Pi_{sol}+\Pi_{ion}\right), \tag{B.4}$$

$$s_r = NkT\left(\lambda_r-\lambda_r^{-1}\right)-\lambda_\theta^2\left(\Pi_{sol}+\Pi_{ion}\right). \tag{B.5}$$

A combination of the above equations, together with the thermodynamic relations (3.11)-(3.15), leads to coupled first-order ordinary differential equations that govern the function $r(R)$ and $s_r(R)$.

Part C: The code of user subroutine for pH-sensitive hydrogels

```
SUBROUTINE UHYPER(BI1,BI2,AJ,U,UI1,UI2,UI3,TEMP,NOEL,
1 CMNAME,INCMPFLAG,NUMSTATEV,STATEV,NUMFIELDV,FIELDV,
2 FIELDVINC,NUMPROPS,PROPS)
C==================================================================
C       User defined hyperelastic material subroutine
C       for gel with Flory-Rehner free-energy function
C       to be used in Abaqus Standard
C------------------------------------------------------------------
C       Material properties to be passed to the subroutine:
C       PROPS(1) - Nv
C       PROPS(2) - chi
C       PROPS(3) - lambda_0     initial swelling
C       PROPS(4) - vC0          ion concentration in external solution
C       PROPS(5) - pKa          dissociation constant
C       PROPS(6) - f            density of PH sensitive monomer
C       State variable:
C       TEMP      - PH0   PH in the solvent outside the gel
C       Set chemical potential of all kinds of ions at vc0 as 0.
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C           The initial value of PH0 and lambda_0 should match each other

C===============================================================

INCLUDE 'ABA_PARAM.INC'

CHARACTER*80 CMNAME

DIMENSION U(2),UI1(3),UI2(6),UI3(6),STATEV(*),FIELDV(*),

              1 FIELDVINC(*),PROPS(*)

Nv = PROPS(1)

chi = PROPS(2)

lambda0 = PROPS(3)

detF0 = lambda0**3

vCcou=PROPS(4)

vNa=0.0602

vCpro=vNa*10.0**(-TEMP)

vCco=vCcou+vCpro

Ka=10**(-PROPS(5))

f=PROPS(6)



U(1) = Nv/2 * ( 1/lambda0*BI1*AJ**(2.0/3.0) - 3/detF0- 2/detF0*(3*LOG(lambda0) +

         LOG(AJ)))-chi/detF0**2/AJ- (AJ-1/detF0)*LOG(AJ/(AJ-1/detF0))

U(2) = 0

UI1(1) = Nv/2/lambda0*AJ**(2.0/3.0)

UI1(2) = 0
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```
UI1(3) = Nv/3/lambda0*BI1*AJ**(-1.0/3.0)+(1-Nv)/AJ/detF0-
         LOG(AJ/(AJ-1/detF0))+chi/(detF0*AJ)**2
UI2 = 0
UI2(3) = -Nv/9/lambda0*BI1*AJ**(-4.0/3.0) -(1-Nv)/AJ**2/detF0+ 1/AJ/(AJ-1/detF0)/detF0-
         2*chi/detF0**2/AJ**3
UI2(5) = Nv/3/lambda0 * AJ**(-1.0/3.0)
UI3 = 0
UI3(4) = -Nv/9/lambda0 * AJ**(-4.0/3.0)
UI3(6) = 4*Nv/27/lambda0*BI1*AJ**(-7.0/3.0)+ 2*(1-Nv)/AJ**3/detF0-
         (2*AJ-1/detF0)/(AJ*(AJ-1/detF0))**2/detF0+ 6*chi/detF0**2/AJ**4
aa=1+vCcou/vCpro
bb=Ka*(vNa)*aa
cc=-(Ka*vNa*f/AJ/detF0+vCpro*vCco)
dd=-Ka*vNa*vCpro*vCco
PP=cc/aa-(bb**2)/3/(aa**2)
QQ=dd/aa-bb*cc/3/aa**2+2*bb**3/27/aa**3
FORM=(QQ/2)**2+(PP/3)**3
IF(FORM.GE.0.0)THEN
vCH=(-QQ/2+FORM**(1.0/2.0))**(1.0/3.0)+(-QQ/2- FORM**(1.0/2.0))**(1.0/3.0)-bb/3/aa
ELSE
R=QQ**2/4-FORM
theta=ATAN2(-2*(-FORM)**(0.5),QQ)
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```
IF(theta.LT.0.0)THEN

 theta=3.1415926+theta

 ENDIF

 vCH=2*R**(1.0/6.0)*cos(theta/3)-bb/3/aa

 ENDIF



 DCDAJ=Ka*vNa*f*(AJ*detF0)**(-2)

 DDCDDAJ=-2*Ka*vNa*f*(AJ*detF0)**(-3)

 DDDCDDDAJ=6*Ka*vNa*f*(AJ*detF0)**(-4)

 DvCHDAJ=-(vCH)*DCDAJ/(3*aa*vCH**2+2*bb*vCH+cc)

 DDvCHDDAJ=-(vCH*DDCDDAJ+2*DCDAJ*DvCHDAJ+2*bb*DvCHDAJ**2+6*aa*

              vCH*DvCHDAJ**2)/(3*aa*vCH**2+2*bb*vCH+cc)

 DDDvCHDDDAJ=-(6*aa*DvCHDAJ**3+18*aa*vCH*DvCHDAJ*DDvCHDDAJ+6

                 * bb*DvCHDAJ*DDvCHDDAJ+3*DCDAJ*DDvCHDDAJ+3*DDCDDAJ*DvCHDAJ

                 + vCH*DDDCDDDAJ)/(3*aa*vCH**2+2*bb*vCH+cc)

 vCA=aa*vCH-vCpro*vCco/vCH

 DvCADAJ=(aa+vCpro*vCco/vCH**2)*DvCHDAJ

 DDvCADDAJ=(aa+vCpro*vCco/vCH**2)*DDvCHDDAJ-2*DvCHDAJ**2*vCpro*vCco/vCH**3

 DDDvCADDDAJ=DDDvCHDDDAJ*(aa+vCpro*vCco/vCH**2)-6*DDvCHDDAJ*

              DvCHDAJ*vCpro*vCco/(vCH**3)+6*vCpro*vCco/(vCH**4)*(DvCHDAJ**3)

 vCAH=f/detF0/AJ-vCA

 DvCAHDAJ=-f/detF0**2/AJ**2-DvCADAJ
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```
 DDvCAHDDAJ=2*f/detF0**3/AJ**3-DDvCADDAJ

 D3vCAHD3AJ=-6*f/detF0**4/AJ**4-DDDvCADDDAJ

 FORM11=log(vCH)+log(vCA)-log(vCAH)-log(vNa)-log(Ka)

 FORM12=aa*vCH+vCpro*vCco/vCH

 FORM21=DvCHDAJ/vCH+DvCADAJ/vCA-DvCAHDAJ/vCAH

 FORM22=(aa-vCpro*vCco/(vCH**2))*DvCHDAJ

 FORM31=DDvCHDDAJ/vCH-(DvCHDAJ/vCH)**2+DDvCADDAJ/vCA-DvCADAJ/vCA)**2-DDvCAHDD
        AJ/vCAH+(DvCAHDAJ/vCAH)**2

 FORM32=(aa-vCpro*vCco/(vCH**2))*DDvCHDDAJ+2*vCpro*vCco/(vCH**3)*(DvCHDAJ**2)

 FORM41=DDDvCHDDDAJ/vCH-3*DDvCHDDAJ*DvCHDAJ/vCH**2
       + 2*(DvCHDAJ/vCH)**3+DDDvCADDDAJ/vCA-3*DDvCADDAJ*DvCADAJ
       / vCA**2+2*(DvCADAJ/vCA)**3-D3vCAHD3AJ/vCAH+3*DDvCAHDDAJ
       * DvCAHDAJ/vCAH**2-2*(DvCAHDAJ/vCAH)**3

 FORM42=(aa-vCpro*vCco/(vCH**2))*DDDvCHDDDAJ+6*vCpro*
         vCco/(vCH**3)*DDvCHDDAJ*DvCHDAJ-6*vCpro*vCco/(vCH**4)* DvCHDAJ**3

 GAJ=detF0*AJ*vCA*FORM11+f*(log(detF0*AJ)-log(f)+log(vCAH))+(detF0*AJ-1)*(vCpro+vCco+
    vCcou)- detF0*AJ*FORM12

 FI=vCpro+vCco+vCcou

 SE=f*(1/(detF0*AJ)+DvCAHDAJ/vCAH)

 TH=(vCA+detF0*AJ*DvCADAJ)*FORM11

 FO=detF0*AJ*vCA*FORM21-FORM12-AJ*detF0*FORM22

 DGDAJ=FI+SE+TH+FO
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```
DDGDDAJ=f*(-1/(detF0*AJ)**2+DDvCAHDDAJ/vCAH-(DvCAHDAJ/vCAH)**2)+*FORM21*(vCA+detF0*
AJ
*DvCADAJ)+FORM11*(2*DvCADAJ+detF0*AJ*DvCADDAJ)+detF0*vCA*AJ*FORM31-2*FORM22-AJ*d
etF0*FORM32


DDDGDDDAJ=f*(2/(detF0*AJ)**3+D3vCAHD3AJ/vCAH-3*DvCAHDAJ*DDvCAHDDAJ/vCAH**2+2*
        (DvCAHDAJ/vCAH)**3)+3*FORM21*(2*DvCADAJ+detF0*AJ*DDvCADDAJ)+3*(vCA+detF0*
AJ
        *DvCADAJ)*FORM31+FORM11*(3*DDvCADDAJ+detF0*AJ*DDDvCADDDAJ)+detF0
        *AJ*vCA*FORM41-3*FORM32-detF0*AJ*FORM42
U(1)=U(1)+GAJ/detF0
UI1(3)=UI1(3)+DGDAJ
UI2(3)=UI2(3)+DDGDDAJ*detF0
UI3(6)=UI3(6)+DDDGDDDAJ*detF0**2


RETURN
END
```

References

1. S.S. Sternstein, *J. Macromol. Sci. Phys B*, 1972, **6**, 243-262.
2. X.H. Zhao, W. Hong, Z.G. Suo, *Appl. Phys. Lett.*, 2008, **92**, 051904.