

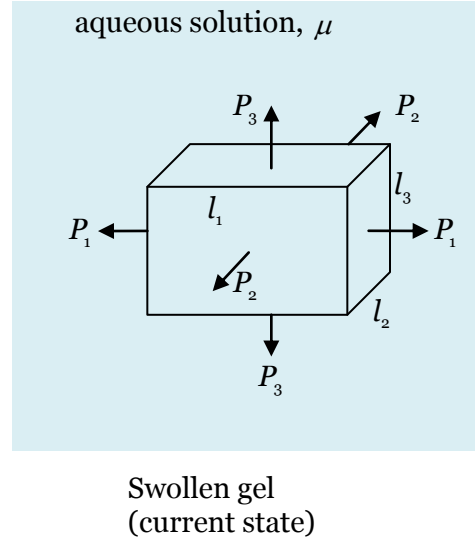
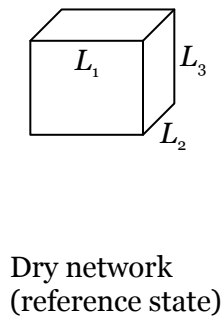
Elastomer in equilibrium with forces and solvent

A long polymer consists of many monomers. The monomers are covalently bonded, and two bonded monomers may rotate relative to each other. Consequently, the polymer may be modeled as a chain of many links, each link representing a monomer. At a finite temperature, the polymer rapidly changes from one configuration to another.

A large number of long, flexible polymers can be crosslinked by covalent bonds to form a three-dimensional network. Subject to forces, the network undergoes large elastic deformation. The network is commonly called an elastomer.

Now immerse the network in an aqueous environment, such as pure liquid water, a moist gas, and aqueous solutions. If the polymers of the network are hydrophilic, the network may imbibe a large quantity of water, and swell greatly. The network and water molecules form an aggregate known as a hydrogel.

The time-dependent process of water migrating in the network is considered in notes on poroelasticity (<http://imechanica.org/node/987>). We now focus on the conditions of equilibrium of the network, the forces, and the aqueous environment.



Condition of equilibrium. Consider a block of an elastomer. In the reference state, the block is a dry network, of dimensions L_1 , L_2 and L_3 . In the current state, the block is a swollen gel, subject to forces P_1 , P_2 and P_3 , submerged in an aqueous solution. We arrange the experiment such that, of all

molecular species, only water molecules will exchange between the gel and the aqueous solution. Let the chemical potential of water in the aqueous solution be μ . See notes on chemical potential (<http://imechanica.org/node/911>). By convention, the chemical potential of water in pure liquid water is set to be zero. In the current state, the block absorbs M number of water molecules, and dimensions of the block become l_1 , l_2 and l_3 .

When the block changes the dimensions by small amounts δl_1 , δl_2 and δl_3 , the potential energy of the forces reduces by $P_1\delta l_1 + P_2\delta l_2 + P_3\delta l_3$; we also say that the forces do work $P_1\delta l_1 + P_2\delta l_2 + P_3\delta l_3$. When the number of water molecules in the block increases by δM , the Helmholtz free energy of the surrounding aqueous solution reduces by $\mu\delta M$; we also say that the chemical potential of water in the surrounding aqueous solution does work $\mu\delta M$. That is, the applied forces are work-conjugate to the displacements, and the chemical potential of water in the surrounding aqueous solution is work-conjugate to the number of water molecules.

Swelling is a highly entropic process. The Helmholtz free energy of the block in the current state is denoted as F . We will consider isothermal process, and will not discuss temperature. At a constant temperature, when the hydrogel equilibrates with the applied forces and the surrounding aqueous solution, the change in the Helmholtz free energy of the block equals the sum of the work done by the applied forces and the work done by the chemical potential of water:

$$\delta F = P_1\delta l_1 + P_2\delta l_2 + P_3\delta l_3 + \mu\delta M.$$

The dimensions of the block, l_1 , l_2 and l_3 , can vary independently from the number of water molecules in the hydrogel, M . The above condition of equilibrium holds for arbitrary and independent small variations of the four independent quantities: l_1 , l_2 , l_3 and M .

This condition of equilibrium can also be interpreted in a different way. The gel, the forces and the surrounding solution together can be viewed as a composite system. The composite is held at a fixed temperature, and receives no work or matter from the rest of the world. The Helmholtz free energy of the composite is the sum of the Helmholtz free energy of the gel, the potential energy of the forces, and the Helmholtz free energy of the surrounding solution. The parameters l_1 , l_2 , l_3 and M are internal variables of the composite system. The condition for the composite to equilibrate is that variation of the Helmholtz free energy of the composite vanishes for arbitrary and independent variations of the internal variables.

We can experimentally measure forces acting on the gel, P_1 , P_2 and P_3 , the chemical potential of water in the surrounding solution, μ , the increments of the dimensions, δl_1 , δl_2 and δl_3 , and the increment of the number of water molecules in the gel, δM . The above condition of equilibrium enables us to determine incrementally the Helmholtz free energy of the gel, F .

Homogeneous field. Assume that, in the current state, the distribution of water in the gel and the deformation of the network is homogeneous. Define the nominal density of the Helmholtz free energy by $W = F/(L_1 L_2 L_3)$, the nominal concentration of water by $C = M/L_1 L_2 L_3$, the stretches by $\lambda_1 = l_1/L_1$, $\lambda_2 = l_2/L_2$ and $\lambda_3 = l_3/L_3$, and the true stresses by $\sigma_1 = P_1/(l_2 l_3)$, $\sigma_2 = P_2/(l_1 l_3)$ and $\sigma_3 = P_3/(l_1 l_2)$.

Dividing both sides of the condition of equilibrium by the volume of the dry elastomer, $L_1 L_2 L_3$, we obtain that

$$\delta W = \sigma_1 \lambda_2 \lambda_3 \delta \lambda_1 + \sigma_2 \lambda_1 \lambda_3 \delta \lambda_2 + \sigma_3 \lambda_1 \lambda_2 \delta \lambda_3 + \mu \delta C.$$

This condition of equilibrium holds for arbitrary and independent variations $\delta \lambda_1$, $\delta \lambda_2$, $\delta \lambda_3$, and δC .

As a material model, the nominal density of the free energy is taken to be a function of the four independent variables:

$$W = W(\lambda_1, \lambda_2, \lambda_3, C).$$

According to the differential calculus, associated with the small changes, $\delta \lambda_1$, $\delta \lambda_2$, $\delta \lambda_3$ and δC , the free energy varies by

$$\delta W = \frac{\partial W}{\partial \lambda_1} \delta \lambda_1 + \frac{\partial W}{\partial \lambda_2} \delta \lambda_2 + \frac{\partial W}{\partial \lambda_3} \delta \lambda_3 + \frac{\partial W}{\partial C} \delta C.$$

A comparison of the two expressions for δW gives that

$$\left(\frac{\partial W}{\partial \lambda_1} - \sigma_1 \lambda_2 \lambda_3 \right) \delta \lambda_1 + \left(\frac{\partial W}{\partial \lambda_2} - \sigma_2 \lambda_1 \lambda_3 \right) \delta \lambda_2 + \left(\frac{\partial W}{\partial \lambda_3} - \sigma_3 \lambda_1 \lambda_2 \right) \delta \lambda_3 + \left(\frac{\partial W}{\partial C} - \mu \right) \delta C = 0.$$

When the gel equilibrates with the external solution and the applied forces, the above equation holds for arbitrary and independent variations $\delta \lambda_1$, $\delta \lambda_2$, $\delta \lambda_3$ and δC . Consequently, the coefficient in front of each of the four variations must vanish, leading to four independent equations:

$$\sigma_1 = \frac{\partial W(\lambda_1, \lambda_2, \lambda_3, C)}{\lambda_2 \lambda_3 \partial \lambda_1},$$

$$\begin{aligned}\sigma_2 &= \frac{\partial W(\lambda_1, \lambda_2, \lambda_3, C)}{\lambda_1 \lambda_3 \partial \lambda_2}, \\ \sigma_3 &= \frac{\partial W(\lambda_1, \lambda_2, \lambda_3, C)}{\lambda_1 \lambda_2 \partial \lambda_3}, \\ \mu &= \frac{\partial W(\lambda_1, \lambda_2, \lambda_3, C)}{\partial C}.\end{aligned}$$

When the function $W(\lambda_1, \lambda_2, \lambda_3, C)$ is specified for a hydrogel, the above equations constitute the equations of state. The four equations of state relate eight variables: $\lambda_1, \lambda_2, \lambda_3, C, \sigma_1, \sigma_2, \sigma_3, \mu$.

Nominal stresses. Instead of the true stresses, we can also use the nominal stresses. Define the nominal stresses by $s_1 = P_1 / (L_2 L_3)$, $s_2 = P_2 / (L_1 L_3)$ and $s_3 = P_3 / (L_1 L_2)$.

Dividing both sides of the condition of equilibrium by the volume of the dry elastomer, $L_1 L_2 L_3$, we obtain that

$$\delta W = s_1 \delta \lambda_1 + s_2 \delta \lambda_2 + s_3 \delta \lambda_3 + \mu \delta C.$$

This condition of equilibrium holds for arbitrary and independent variations $\delta \lambda_1$, $\delta \lambda_2$, $\delta \lambda_3$, and δC .

$$\begin{aligned}s_1 &= \frac{\partial W(\lambda_1, \lambda_2, \lambda_3, C)}{\partial \lambda_1}, \\ s_2 &= \frac{\partial W(\lambda_1, \lambda_2, \lambda_3, C)}{\partial \lambda_2}, \\ s_3 &= \frac{\partial W(\lambda_1, \lambda_2, \lambda_3, C)}{\partial \lambda_3}, \\ \mu &= \frac{\partial W(\lambda_1, \lambda_2, \lambda_3, C)}{\partial C}.\end{aligned}$$

Additive volumes (molecular incompressibility). In the above, we have assumed that l_1 , l_2 , l_3 and M vary independently. In practice, however, the four quantities are connected by the following considerations. Upon imbibing water, the network swells. The two processes—imbibing and swelling—are connected. The volume of the block in the current state $l_1 l_2 l_3$, to a good approximation, equals the sum of the volume of the dry network $L_1 L_2 L_3$ and the

volume of the absorbed water νM , where ν is the volume per water molecule. Write

$$l_1 l_2 l_3 = L_1 L_2 L_3 + \nu M,$$

where ν is the volume per water molecule.

This approximation is commonly adopted in analyzing the swelling process of gels. The approximation generalizes the condition of incompressibility of elastomers, and is called molecular incompressibility (Hong, Zhao, Zhou and Suo, *J. Mech. Phys. Solids* 56, 1779, 2008). The approximation may be justified by the following considerations.

The network consists of long and flexible polymer chains, which interact among themselves and with water molecules by weak intermolecular forces. When water molecules enter the block, the polymer chains stretch and move apart to accommodate the water molecules. When water molecules migrate out the gel, the polymer chains coil back and move together, leaving no voids behind. In this regard, a gel differs from a sponge. When water leaves a sponge, pores in the sponge remain open and are filled by air.

The forces applied to the hydrogel are typically small, and do not appreciably change the volumes of individual polymer chains or water molecules.

When two species of molecules mix, the volume of the mixture usually differs from the sum of the volumes of the two pure components. This change in volume, however, is typically small compared to the change in volume during swelling.

Dividing both sides of the above equation by the volume of the dry elastomer, $L_1 L_2 L_3$, we obtain that

$$\lambda_1 \lambda_2 \lambda_3 = 1 + \nu C.$$

This expression places a constraint among the four variables: λ_1 , λ_2 , λ_3 and C . We regard λ_1 , λ_2 and λ_3 as independent variables. In terms of the stretches, the variation of the concentration is

$$\delta C = \frac{\lambda_2 \lambda_3}{\nu} \delta \lambda_1 + \frac{\lambda_1 \lambda_3}{\nu} \delta \lambda_2 + \frac{\lambda_1 \lambda_2}{\nu} \delta \lambda_3.$$

Equations of state consistent with molecular incompressibility.

Inserting this expression into the condition of equilibrium, we obtain that

$$\delta W = \left(\sigma_1 + \frac{\mu}{\nu} \right) \lambda_2 \lambda_3 \delta \lambda_1 + \left(\sigma_2 + \frac{\mu}{\nu} \right) \lambda_1 \lambda_3 \delta \lambda_2 + \left(\sigma_3 + \frac{\mu}{\nu} \right) \lambda_1 \lambda_2 \delta \lambda_3.$$

This condition of equilibrium holds for arbitrary and independent variations $\delta \lambda_1$, $\delta \lambda_2$ and $\delta \lambda_3$.

As a material model, the nominal density of the free energy is taken to be a function of four independent variables:

$$W = W(\lambda_1, \lambda_2, \lambda_3).$$

Due to the constraint $\lambda_1 \lambda_2 \lambda_3 = 1 + \nu C$, the concentration of water is excluded from the list of the independent variables. According to the differential calculus, when the block deforms by small amounts, $\delta\lambda_1$, $\delta\lambda_2$ and $\delta\lambda_3$, the free energy varies by

$$\delta W = \frac{\partial W}{\partial \lambda_1} \delta \lambda_1 + \frac{\partial W}{\partial \lambda_2} \delta \lambda_2 + \frac{\partial W}{\partial \lambda_3} \delta \lambda_3.$$

A comparison of the two expressions for δW gives that

$$\left[\frac{\partial W}{\partial \lambda_1} - \left(\sigma_1 + \frac{\mu}{\nu} \right) \lambda_2 \lambda_3 \right] \delta \lambda_1 + \left[\frac{\partial W}{\partial \lambda_2} - \left(\sigma_2 + \frac{\mu}{\nu} \right) \lambda_1 \lambda_3 \right] \delta \lambda_2 + \left[\frac{\partial W}{\partial \lambda_3} - \left(\sigma_3 + \frac{\mu}{\nu} \right) \lambda_1 \lambda_2 \right] \delta \lambda_3 = 0.$$

When the hydrogel equilibrates with the surrounding aqueous solution and the applied forces, this equation holds for arbitrary and independent variations $\delta\lambda_1$, $\delta\lambda_2$ and $\delta\lambda_3$. Consequently, the coefficient in front of each of the three variations must vanish, leading to three independent equations:

$$\begin{aligned} \sigma_1 &= \frac{\partial W(\lambda_1, \lambda_2, \lambda_3)}{\lambda_2 \lambda_3 \partial \lambda_1} - \frac{\mu}{\nu}, \\ \sigma_2 &= \frac{\partial W(\lambda_1, \lambda_2, \lambda_3)}{\lambda_1 \lambda_3 \partial \lambda_2} - \frac{\mu}{\nu}, \\ \sigma_3 &= \frac{\partial W(\lambda_1, \lambda_2, \lambda_3)}{\lambda_1 \lambda_2 \partial \lambda_3} - \frac{\mu}{\nu}. \end{aligned}$$

These equations, along with $\lambda_1 \lambda_2 \lambda_3 = 1 + \nu C$, constitute the equations of state.

The four equations of state relate eight variables: $\lambda_1, \lambda_2, \lambda_3, C, \sigma_1, \sigma_2, \sigma_3, \mu$.

The equations of state describe the mechanochemical interaction of the hydrogels. In particular, the term μ/ν has the dimension of stress, and is known as the pore pressure in poroelasticity, and as the water potential in plant physiology. The effect of μ/ν is readily understood by considering a block of a hydrogel confined in a rigid and porous box. The box constrains the hydrogel to fixed dimensions, but the box is permeable to water. When the chemical potential of water in the surrounding aqueous solution is increased, to keep the dimensions of the gel fixed, the gel develops an additional pressure.

Superposing models of elasticity and models of solutions. We now discuss a particular way to specify the nominal density of the Helmholtz free

energy as a function of stretches, $W(\lambda_1, \lambda_2, \lambda_3)$. When the polymers are not crosslinked, individual polymeric molecules may dissolve in water. A large number of models of polymer-solvent solutions exist. When the polymers are crosslinked, the network acquires entropic elasticity. A large number of models of elasticity exist.

In many gels, the density of the crosslinks is very low. For example, each polymer chain may consist of over a thousand monomers. Consequently, to the first approximation, we may neglect the effect of the crosslinks on solution, and simply write the free energy of the gel as the sum:

$$W = W_{stretch} + W_{mix},$$

where $W_{stretch}$ is the free energy due to the stretching of the network, and W_{mix} is the free energy due to the mixing of the polymers and the solvent.

Flory-Rehner model. The best known model of this kind is due to Flory and Rehner (J. Chem. Phys. 11, 521-526, 1943). In this model, the free energy due to the stretching of the network of polymers is taken to be

$$W_{stretch} = \frac{1}{2} NkT (\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3 - 2 \log \lambda_1 \lambda_2 \lambda_3),$$

where N is the number of polymer chains in the gel divided by the volume of the dry polymers, and kT is the temperature in the unit of energy.

When the long polymers are not cross-linked, the long polymers and the small molecules form a liquid solution. The free energy of mixing is taken to be (Flory, 1942; Huggins, 1941)

$$W_{mix} = -\frac{kT}{v} \left[vC \log \left(1 + \frac{1}{vC} \right) + \frac{\chi}{1 + vC} \right].$$

The first term in the bracket comes from the entropy of mixing, and the second from the energy of mixing, where χ is a dimensionless parameter. The energy of mixing motivates the small molecules to enter the gel if $\chi < 0$, but motivates the small molecules to leave the gel if $\chi > 0$.

Using the nominal density of free energy of the Flory-Rehner model, we obtain that

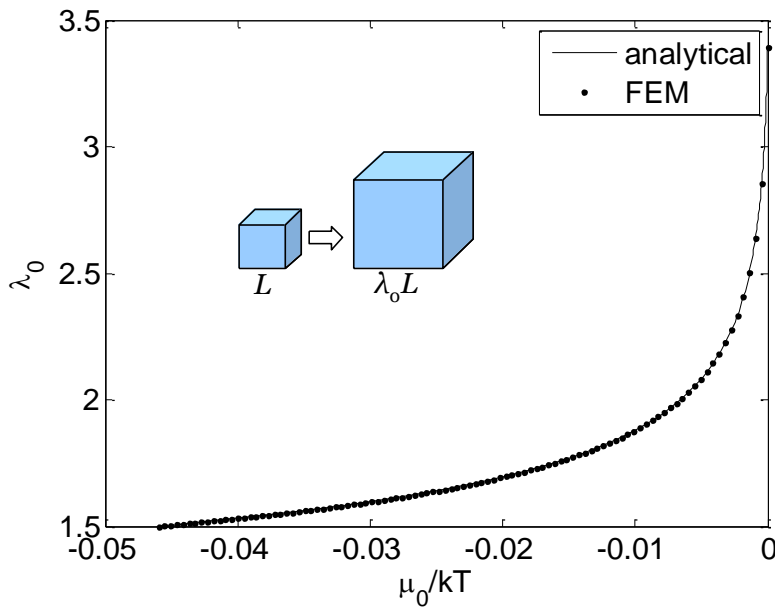
$$\sigma_1 = \frac{NkT}{\lambda_2 \lambda_3} (\lambda_1 - \lambda_1^{-1}) + \frac{kT}{v} \left[\log \left(1 - \frac{1}{\lambda_1 \lambda_2 \lambda_3} \right) + \frac{1}{\lambda_1 \lambda_2 \lambda_3} + \frac{\chi}{(\lambda_1 \lambda_2 \lambda_3)^2} \right] - \frac{\mu}{v}.$$

Expressions for the other two components of stress can be obtained by permutation. Within the Flory-Rehner model, each term in the above equation has a clear molecular interpretation. We have already discussed the last term.

The term scaling with NkT comes from stretching the network. The term scaling with kT/v comes from mixing the network and the solvent. The entropy of mixing motivates water to migrate into the network. The energy of mixing either motivates water to migrate wither into or out of the network, depending on the sign of χ .

The volume of a water molecule is $v = 3 \times 10^{-29} \text{ m}^3$. At room temperature, $kT = 4 \times 10^{-21} \text{ J}$ and $kT/v = 1.3 \times 10^8 \text{ Pa}$. The Flory-Rehner free-energy function introduces two dimensionless material parameters: Nv and χ . In the absence of solvent molecules, the dry network have a shear modulus NkT under the small-strain conditions, with the representative values $NkT = 1 \text{ } \sigma^4 \sim 1 \text{ } \sigma \text{ N/m}^2$, which gives the range $Nv = 10^{-4} \sim 10^{-1}$. The parameter χ is a dimensionless measure of the enthalpy of mixing, with representative values $\chi = 0 \sim 1.2$. For applications that prefer gels with large swelling ratios, materials with low χ values are used.

Exercise. Derive the above expression for stress.



Free swelling. The following two sections are taken from Hong, Liu and Suo (Int. J. Solids and Structure 46, 3282, 2009). A cubic block of a gel is immersed in an aqueous solution. The chemical potential of water in the

solution is μ_0 . Relative to the dry network, the network in this state swells with isotropic stretches: $\lambda_1 = \lambda_2 = \lambda_3$. We denote this free-swelling stretch by λ_0 . Setting stress to be zero, we obtain that

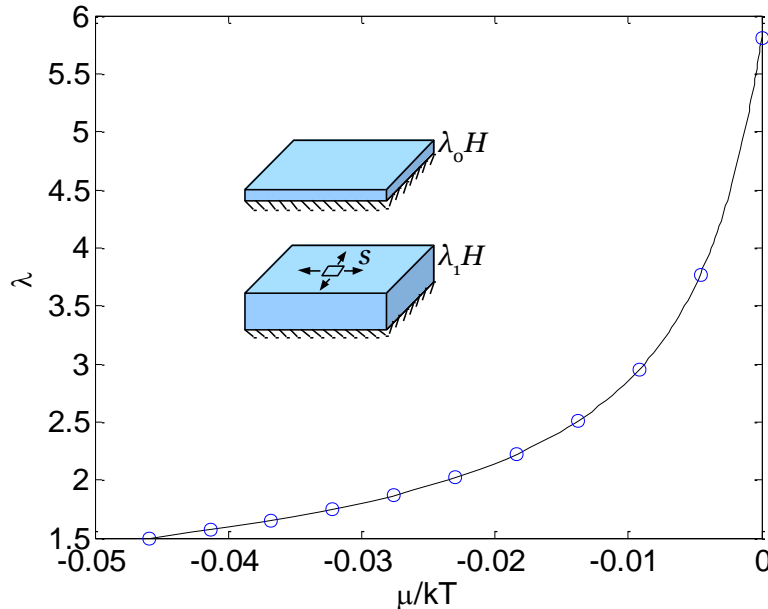
$$N\nu\left(\frac{1}{\lambda_0} - \frac{1}{\lambda_0^3}\right) + \log\left(1 - \frac{1}{\lambda_0^3}\right) + \frac{1}{\lambda_0^3} + \frac{\chi}{\lambda_0^6} = \frac{\mu_0}{kT}.$$

This equation relates the free-swelling stretch to the chemical potential of water. In plotting the figure, we will use the values $N\nu = 10^3$ and $\chi = 0.1$.

Constrained swelling. A layer of a gel is fabricated on a rigid substrate, with stress-free pre-swelling of isotropic stretch $\lambda_0 = 1.5$. Subsequently, the gel is brought into contact with a solvent with chemical potential μ . The gel swells further to a stretch λ in the direction normal to the layer, and develops a state of equal-biaxial stress s . The stress normal to the layer vanishes, so that

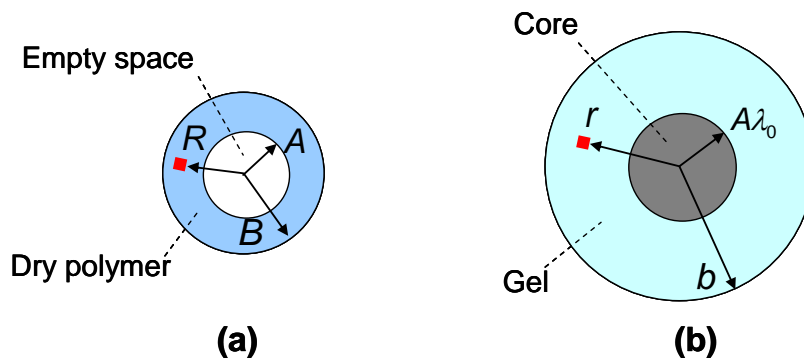
$$\frac{N\nu}{\lambda_0^2}\left(\lambda - \frac{1}{\lambda}\right) + \log\left(1 - \frac{1}{\lambda_0^2\lambda}\right) + \frac{1}{\lambda_0^2\lambda} + \frac{\chi}{(\lambda_0^2\lambda)^2} = \frac{\mu}{kT}.$$

where the two in-plane stretches are constrained by rigid substrate to be the initial value λ_0 , but the out-of-plane stretch λ can vary with the chemical potential.



A spherical gel with a rigid core. This section is taken from X.H. Zhao, W. Hong, Z.G. Suo, Inhomogeneous and anisotropic equilibrium state of a swollen hydrogel containing a hard core. Applied Physics Letters 92, 051904 (2008).

Consider a core-shell structure. A water-free and stress-free polymeric network is taken as the reference state, where the network is a hollow spherical shell, with inner radius A and outer radius B . This reference state, however, is usually not the state in which the structure is prepared. Here we assume that the structure is prepared by first coating a hard core, radius $A\lambda_0$, with a shell of a solution with a certain fraction of water, and then cross-linking the polymers in the solution. The structure is then immersed in a solvent to imbibe more water. After some time, water molecules in the gel equilibrate those in the external solvent, and the gel swell to an inhomogeneous and anisotropic state. This behavior is readily understood as follows. The core is taken to be rigid and bonded to the network, so that near the interface the network cannot further stretch in the circumferential directions, and is constrained to swell only in the radial direction. Away from the interface, the network can stretch in all three directions, but by different amounts. The inhomogeneity in deformation corresponds to an inhomogeneous distribution of water in the gel: the concentration of water is expected to be low near the interface, and increases in the gel away from the interface.



Reference State

Equilibrium State

This state of inhomogeneous and anisotropic deformation can be determined by solving a boundary value problem. Imagine an element of the network is labeled by the radius R in the reference state, and moves to a place of the radius r in the equilibrium state. The deformed gel is taken to retain the spherical symmetry, so that the state of deformation is fully specified by the function $r(R)$.

Markers on a spherical surface of radius R in the reference state move to a spherical surface of radius r in the equilibrium state. Consequently, the stretch in each of the circumferential directions is

$$\lambda_\theta = \frac{r}{R}$$

Two nearby markers in the same radius direction, of positions R and $R+dR$ in the reference state, move to positions $r(R)$ and $r(R+dR)$ in the equilibrium state. The distance between the two markers is dR in the reference state, and is $r(R+dR)-r(R)=dr$ in the equilibrium state, so that the stretch in the radial direction is

$$\lambda_r = \frac{dr}{dR}$$

An element of the network, of unit volume in the reference state, swells to volume $\lambda_\theta^2 \lambda_r$ in the equilibrium state. Both the polymers and water molecules are taken to be incompressible. Consequently, the change in volume of the gel is due to imbibing water molecules:

$$vC = \lambda_\theta^2 \lambda_r - 1,$$

where v is the volume per solvent molecule, and C is the concentration of water in the gel (i.e., the number of water molecules in an element of the gel in the equilibrium state divided by the volume of the element in the reference state).

Due to constraint, the gel develops a field of stress in the equilibrium state. Let s_θ be the nominal stress in each of the circumferential directions, and s_r be the nominal stress in the radial direction. The stresses are functions of the position R . Mechanical equilibrium requires that

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

Denote the chemical potential of water in the environment by μ , which is held constant as the gel imbibes water. When water molecules in the environment equilibrates with those in the gel, the chemical potential of water in the gel is also μ . Both the chemical potential and the stretches cause stresses in the gel

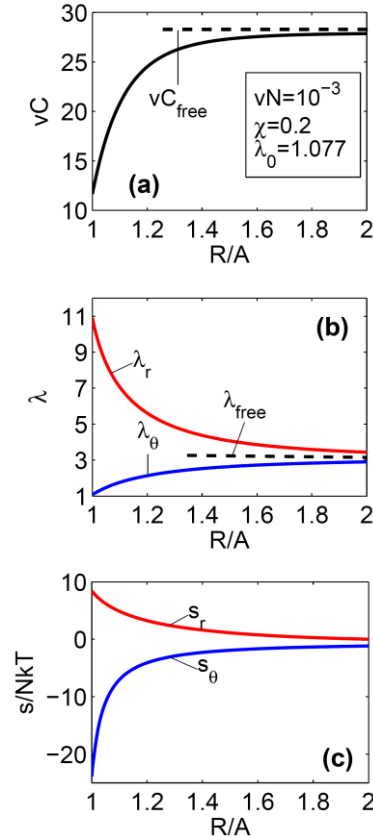
$$\begin{aligned} \frac{vs_\theta}{kT} &= vN(\lambda_\theta - \lambda_\theta^{-1}) - \left(\frac{\mu}{kT} - g \right) \lambda_\theta \lambda_r, \\ \frac{vs_r}{kT} &= vN(\lambda_r - \lambda_r^{-1}) - \left(\frac{\mu}{kT} - g \right) \lambda_\theta^2, \end{aligned}$$

where N is the number of polymeric chains in the gel divided by the volume of the dry polymers, kT is the temperature in the unit of energy, and

$$g = \left[\log \frac{vC}{1+vC} + \frac{1}{1+vC} + \frac{\chi}{(1+vC)^2} \right],$$

with χ being a dimensionless measure of the enthalpy of mixing.

In the numerical results, we set $vN=10^3$, $\chi=0.2$, $B/A=2$, and $\lambda_0=1.077$. As shown in the figure, the concentration of water in the gel (i.e., the ratio of the volume of water to that of the dry network, vC) increases from ~ 12 at the interface to ~ 28 at the outer surface. The concentration of water near the outer surface is close to that in a free-swelling gel, a level that is marked as the dashed line. Evidently the effect of the constraint on the gel is localized within a radius only slightly larger than the radius of the core. Near the interface, the stretch λ_θ is constrained by the core and does not change during swelling, but λ_r increases substantially. Near the outer surface, both stretches approach that of a free-swelling gel. Near the interface, s_θ is compressive, but s_r is tensile. Both stresses diminish near the outer surface. The tensile radial stress may cause the gel to debond from the core.



Exercise. Formulate a similar problem of cylindrical symmetry. This problem has been considered as a model for swellable packers for oilfield management. See Cai, Lou, Ganguly, Robisson, Suo, *J. Appl. Phys.* 107, 103535 (2010).

Inhomogeneous deformation of a gel in equilibrium with external forces and solution. The above example illustrates inhomogeneous deformation in the gel. Now we consider a general formulation of inhomogeneous deformation. A network imbibes water from a field of pumps. To attain a state of equilibrium, the chemical potential of water in all the pumps must be equal, and is denoted by μ . We also hang a field of weights on the network. After some time, the network is saturated with water, in equilibrium with the pumps and the weights. In this state of equilibrium, the deformation of

the network can be inhomogeneous. We formulate a theory to determine the field of inhomogeneous deformation.

Kinematics of the network. We take any state of the network as a reference state, and name a material particle in the network using its coordinates \mathbf{X} in the reference state. In the current state at time t , the material particle \mathbf{X} is at a place with coordinate \mathbf{x} . The function $\mathbf{x}(\mathbf{X})$ describes the deformation of the network.

For inhomogeneous deformation in three dimensions, the stretch is generalized to the deformation gradient

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

Conservation of the number of water molecules. Consider a block of the network around \mathbf{X} , of volume $dV(\mathbf{X})$. Let $C(\mathbf{X})dV(\mathbf{X})$ be the number of water molecules in block when the gel is in the current state. That is, $C(\mathbf{X})$ is the nominal concentration of water in the gel in the current state.

Associated with a small change in the concentration, $\delta C(\mathbf{X})$, the pumps inject into the gel the following number of water molecules:

$$\int \delta C dV.$$

Free energy of the gel. Let W be the nominal density of free energy of the gel, namely, the free energy in a block in the current state divided by the volume of the block in the reference state. Thus, the free energy of the gel is

$$\int w dV.$$

As a material model, we assume that the nominal density of the free energy is a function of the deformation gradient and the concentration,

$$W = W(\mathbf{F}, C).$$

To ensure that the free energy is unchanged when the body undergoes a rigid-body rotation, we requires that W depends on \mathbf{F} through the Green deformation tensor $F_{iK}F_{iL}$.

Associated with any virtual changes, δF_{iK} and δC , the nominal density of free energy changes by

$$\delta W = \frac{\partial W(\mathbf{F}, C)}{\partial F_{iK}} \delta F_{iK} + \frac{\partial W(\mathbf{F}, C)}{\partial C} \delta C.$$

Work done by a field of weights. Consider a block of the network around \mathbf{X} , of volume $dV(\mathbf{X})$. Let $dA(\mathbf{X})$ be the area of an element of the surface of the gel, and $N_K(\mathbf{X})$ be the unit vector normal to the element. We hang weights on to

the network. Let $\mathbf{B}(\mathbf{X}, t)dV(\mathbf{X})$ be the force due to the weights on a material element of volume, and $\mathbf{T}(\mathbf{X}, t)dA(\mathbf{X})$ be the force due to the weights on a material element of interface. Associated with a deformation of the network, $\delta\mathbf{x}(\mathbf{X})$, the weights do work

$$\int B_i \delta x_i dV + \int T_i \delta x_i dA.$$

The free energy of the weights reduces by this amount.

Work done by a field of pumps. Associated with a small change in the concentration, $\delta C(\mathbf{X})$, the field of pumps do work

$$\mu \int \delta C dV.$$

The gel in equilibrium with the weights and the pumps. When the gel equilibrates with the weights and the pumps, the change in the free energy in the gel equals the sum of the work done by the weights and the pumps, namely,

$$\int \delta W dV = \int B_i \delta x_i dV + \int T_i \delta x_i dA + \mu \int \delta C dV.$$

Inserting the expression for δW into the above, and applying the divergence theorem, we obtain that

$$\int \left[\frac{\partial W}{\partial F_{iK}} N_K - T_i \right] \delta x_i dA - \int \left[\frac{\partial}{\partial X_K} \left(\frac{\partial W}{\partial F_{iK}} \right) + B_i \right] \delta x_i dV + \int \left[\frac{\partial W}{\partial C} - \mu \right] \delta C dV = 0.$$

In equilibrium, this equation holds for arbitrary small changes in the deformation and the concentration. Thus, we obtain the equilibrium conditions:

$$\mu = \frac{\partial W(\mathbf{F}, C)}{\partial C}$$

in the volume,

$$\frac{\partial}{\partial X_K} \left(\frac{\partial W}{\partial F_{iK}} \right) + B_i = 0$$

in the volume, and

$$\frac{\partial W}{\partial F_{iK}} N_K = T_i,$$

on the surface. These equations express momentum balance in every current state in terms of the nominal fields, and is well known in continuum mechanics.

Exercise. Write the free energy in the Flory-Rehner model as a function $W(\mathbf{F}, C)$.

Chemical potential as an independent variable. Because the

chemical potential of water in the pumps is prescribed, it will be convenient to regard μ as an independent variable. Take the Lagendre transformation:

$$\hat{W} = W - C\mu,$$

In equilibrium, the new free energy is a function of the deformation gradient and chemical potential, namely,

$$\hat{W} = \hat{W}(\mathbf{F}, \mu).$$

The differential form of the function is

$$\delta\hat{W} = s_{iK}\delta F_{iK} - C\delta\mu,$$

so that

$$s_{iK} = \frac{\partial\hat{W}(\mathbf{F}, \mu)}{\partial F_{iK}},$$

$$-C = \frac{\partial\hat{W}(\mathbf{F}, \mu)}{\partial\mu}.$$

Summary of equations. Let us summarize the basic equations suitable for solving boundary-value problems. The deformation gradient is defined as

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

The thermodynamic model of the gel is prescribed by the function

$$\hat{W} = \hat{W}(\mathbf{F}, \mu).$$

The stress relates to the partial derivative

$$s_{iK} = \frac{\partial\hat{W}(\mathbf{F}, \mu)}{\partial F_{iK}}.$$

The conditions for mechanical equilibrium become

$$\frac{\partial s_{iK}}{\partial X_K} + B_i = \mathbf{0}$$

in the volume, and

$$s_{iK}N_K = T_i$$

on the surface.

In equilibrium, the chemical potential of water in the gel is uniform, and equals the chemical potential of water in the external solution. The stress in the gel, however, is usually nonuniform. The above equations specify a boundary-value problem that determines $x_i(\mathbf{X})$. This boundary-value problem of the gel looks identical to that of an elastic body.

Once the deformation field $x_i(\mathbf{X})$ is determined, the concentration field is determined by

$$-C = \frac{\partial \hat{W}(\mathbf{F}, \mu)}{\partial \mu}.$$

Additive volumes (molecular incompressibility). Under most types of load, the polymers and the water molecules can undergo large configurational change without appreciable volumetric change. Following a common practice, we assume that the individual polymers and the individual water molecules are incompressible. Furthermore, the gel is a condensed matter with negligible void space, so that we express the condition of molecular incompressibility as

$$1 + \nu C = \det(\mathbf{F}),$$

where ν is the volume per water molecule, and νC is the volume of the water molecules in the gel divided by the volume of the dry network.

Exercise. Write the free energy in the Flory-Rehner model as a function $\hat{W}(\mathbf{F}, \mu)$. Assume molecular incompressibility.

Exercise. Continue the above exercise, and express stresses in terms of the deformation gradient and the chemical potential of water. First use the nominal stress, and then use the true stress.

Finite element method to study large inhomogeneous deformation in gels. Let us summarize the basic equations in a way suitable for finite element analysis. The deformation gradient is defined as

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

The thermodynamic model of the gel is prescribed by the function

$$W = W(\mathbf{F}, C).$$

Introduce a new function:

$$\hat{W} = W - \mu C.$$

The new function is regarded as $\hat{W}(\mathbf{F}, \mu)$.

Recall the condition of equilibrium:

$$\int \delta W dV = \int B_i \delta x_i dV + \int T_i \delta x_i dA + \mu \int \delta C dV.$$

In terms of the function \hat{W} , the condition of equilibrium becomes that the following equation

$$\int \delta \hat{W} dV = \int B_i \delta x_i dV + \int T_i \delta x_i dA$$

holds for arbitrary small change δx_i .

A finite element method has been implemented in ABAQUS by Hong, Liu and Suo (Int. J. Solids and Structure 46, 3282, 2009). The computer code is posted online, <http://imechanica.org/node/3163>.

Opportunities to study gels in equilibrium. Despite a large number of commentaries in the literature to this day, the above theory has remained unchanged since the time of Gibbs (1878). Given that the theory has been implemented within ABAQUS, the opportunities are of two kinds:

- Construct material models by writing out the function $W(\mathbf{F}, C)$ for a given gel, usually through a combination of experiments and microscopic modeling.
- Apply the theory to important phenomena, by formulating and solving boundary-value problems.
- Extend the theory to include variations other than the deformation of the network and the distribution of the solvent. As example, see the theory of polyelectrolyte gels (<http://imechanica.org/node/1690>).

Appendix: Is osmotic pressure a valid idea for gels? Osmotic pressure is a measurable quantity in a liquid solution, but is not a measurable quantity in a gel. Whether osmotic pressure is a valid idea for a gel depends how different the gel is from a liquid solution. Here we outline the basic considerations.

In the above expression for stress, the term due to mixing is sometimes called osmotic pressure or swelling pressure. Consider a special case where the gel is in contact with pure water and swells freely, namely, $\mu = 0$ and $\sigma_1 = \sigma_2 = \sigma_3 = 0$. In this case, the osmotic pressure is balanced by the tension due to the stretching of the network.

In a liquid solution, osmosis occurs when the solution is separated from a pure solvent by a semi-permeable membrane, which lets the solvent to go through, but not the solute. Consequently, the solvent molecules from the pure solvent permeate through the membrane and go into the solution and dilute the solution. The process will stop when a pressure builds up in the solution to counteract the driving force for dilution.

In a gel, polymers are crosslinked. Consequently, even without a semi-permeable membrane, the polymers cannot leave the gel, but the solvent can enter the gel. That is, the crosslinks serve the function of semi-permeable

membrane.

While the notion of osmosis is intuitive for gels, the separation of the stress into a term due to elasticity and a term due to osmosis may cause confusion. The separation is meaningful to idealized models that superpose the free energy of stretching the network and the free energy of mixing the network and the solvent. Such separation, however, is impossible in more general models.

Experimentally, when the polymers are crosslinked, one can measure the chemical potential of water and the applied forces, but cannot measure anything like osmotic pressure. For example, in the special case $\mu = 0$ and $\sigma_1 = \sigma_2 = \sigma_3 = 0$, we can measure how much the gel swells, but no experiment will tell us what osmotic pressure is.

When the polymers are not crosslinked, however, the polymers and the solvent molecules form a liquid solution, and we can measure osmotic pressure in the liquid solution separated from a pure solvent by a semi-permeable membrane. Subsequently, if one assumes that crosslinks do not affect osmosis, but simply imparts elasticity to the network, one can superpose osmosis of the liquid solution and elasticity of the network, just as done in the Flory-Rehner model.