

Poroelasticity, or diffusion in elastic solids

Migration of matter in an elastic solid. A sponge is a porous and elastic solid. When immersed in water, the sponge absorbs water. When a saturated sponge is squeezed, water comes out. Phenomena of this type are analyzed by using a theory known variously as elasticity of a porous solid filled with a fluid, diffusion in an elastic solid, and poroelasticity. The theory has been applied to diverse phenomena. Sketched below are several examples.

Solids that absorb fluids. In his long paper, *On the Equilibrium of Heterogeneous Substances*, Gibbs (1978) considered an elastic solid in equilibrium with a fluid. The solid is elastic, and the fluid is mobile inside the solid. He derived the conditions of equilibrium in terms of deformation gradient, nominal stress, and chemical potential.

His paper is collected in the volume *The Scientific Papers of J. Willard Gibbs*. The book is available in libraries, and is in print. Digital copy of the book is freely available at <http://books.google.com/>. Sections of direct relevance to poroelasticity include

- The conditions of internal and external equilibrium for solids in contact with fluids with regard to all possible states of strain of the solids, p. 184.
- Fundamental equations for solids, p. 201.
- Concerning solids which absorb fluids, p. 215.

Consolidation of soils. A soil is a mixture of solid particles and water. The solid particles are more or less bound together and constitute an elastic skeleton. The interstices of the skeleton are filled with water. When a load is applied to the soil, water flows out gradually, so that the soil deforms over some time. This process is known as consolidation. Biot's 1941 paper is very readable, and is widely considered as a founding paper of poroelasticity. His basic theory has remained unchanged. You may wish to read his paper before reading anything else on the subject.

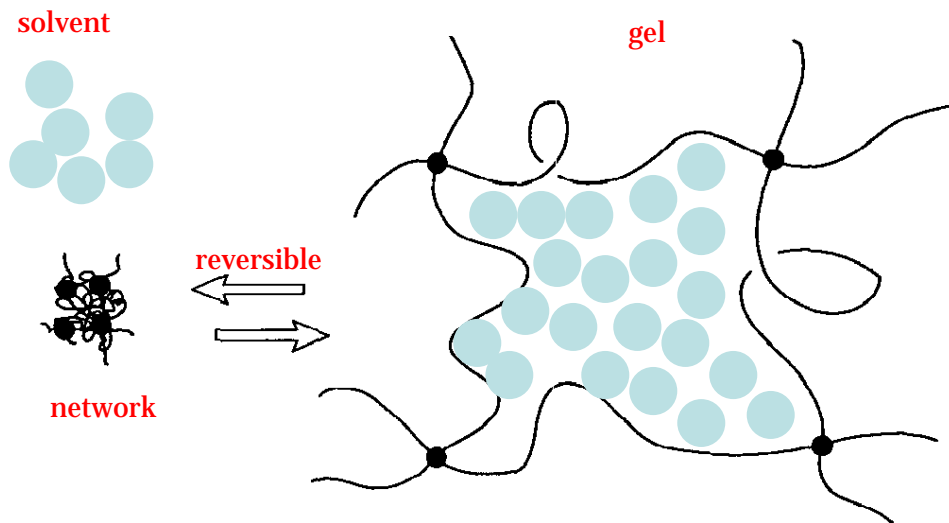
- M.A. Biot, General theory of three-dimensional consolidation, *Journal of Applied Physics* 12, 155-164 (1941).
- E. Detournay and A. H.-D, Cheng, *Fundamentals of Poroelasticity* (<http://www.olemiss.edu/sciencenet/poronet/fundporo.pdf>).
- J.R. Rice, Elasticity of fluid-infiltrated porous solids, notes for teaching on hydrology and environmental geomechanics (http://esag.harvard.edu/rice/e2_Poroelasticity.pdf).
- J. Bear, *Dynamics of fluids in porous media*. Dover reprint, 1988.
- H. F. Wang, *Theory of linear poroelasticity with applications to geomechanics and hydrogeology*. Princeton University Press, 2000.

Swelling gels. A large quantity of small molecules may migrate into a network of long polymers, causing the network to swell, forming an aggregate known as a polymeric gel. When the solvent is water, the gel is called a hydrogel. The polymers are flexible and crosslinked by strong bonds, enabling large and

reversible deformation. The small molecules interact with each other and with polymers by weak bonds, enabling transport.

As the small molecules mix with the long polymers, the network swells, so that the configurational entropy of the network decreases, but the configurational entropy of the mixture increases. Their compromise tends to equilibrate the gel and the solvent, setting the equilibrium swelling ratio. For a review of the literature, see

- W. Hong, X.H. Zhao, J.X. Zhou and Z.G. Suo, A theory of coupled diffusion and large deformation in polymeric gels. *Journal of the Mechanics and Physics of Solids* 56, 1779-1793 (2008).



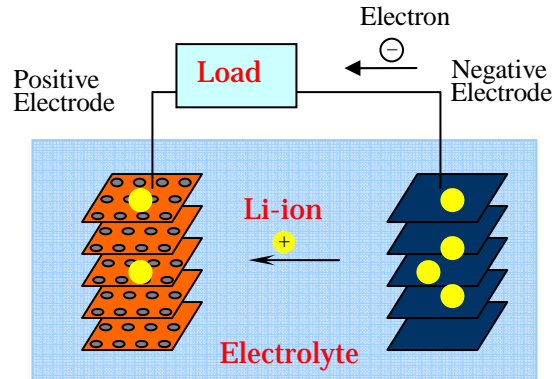
Tissues of animals and plants. Many tissues consist of elastic network and mobile molecules. The elasticity enables the tissues to retain shapes and deforms, while mobile molecules enable the tissues to transport nutrients and wastes.

- S.C. Cowin and S.B. Doty, *Tissue mechanics*. Springer, 2007.

Li-ion Batteries. A battery converts energy between two forms, chemical and electrical. Lithium can diffuse into and react with nearly all materials. A material that conducts electrons may in principle serve as an *electrode*. When two electrodes are in direct contact, lithium atoms diffuse from the electrode with a high chemical potential of lithium (i.e., the negative electrode) to the electrode with a low chemical potential of lithium (i.e., the positive electrode).

In a battery, however, the two electrodes are separated by an *electrolyte*, a material that conducts Li-ions but insulates electrons. When the battery discharges, the difference in the chemical potential of lithium in the two electrodes drives Li-ions to diffuse out of the negative electrode, through the

electrolyte, and into the positive electrode. To keep the electrodes electrically neutral, electrons flow through an external circuit from the negative to the positive electrode. Both the ionic and the electronic processes are reversed when the battery is charged by an external power source.



At the heart of a Li-ion battery is a problem of mechanics. Each electrode consists of host atoms and guest atoms (lithium atoms). The host atoms form a framework, into which lithium atoms are inserted. During charge and discharge, the amount of Li in the electrode varies substantially, and the host framework *deforms*.

The insertion-induced deformation in electrodes has significant consequences in Li-ion batteries. The deformation is often constrained due to crystalline grains of different orientations, transient distribution of lithium, mismatch between active and inactive materials, etc. Under such constraints, insertion of lithium induces in an electrode a field of stress, which may lead to fracture or morphological change. Such mechanical degradation is a significant mechanism that over charge/discharge cycles can cause the capacity of a battery to fade.

- Christensen J, Newman J, 2005. A Mathematical Model of Stress Generation and Fracture in Lithium Manganese Oxide, *Journal of The Electrochemical Society*, 153(6), A1019-A1030.
- Zhang XC, Shyy W, Sastry AM, 2007. Numerical Simulation of Intercalation-Induced Stress in Li-Ion Battery Electrode Particles, *Journal of The Electrochemical Society* 154, A910-A916.

Diffusion in metallic solutions. In a metallic solution, one species of atoms may diffuse much faster than the other, so that the slow diffusers may serve the role of an elastic network. For example, some materials can absorb and release large amounts of hydrogen, making them candidates for [hydrogen storage technology](#).

- F.C. Larche and J.W. Cahn, The interactions of composition and stress in crystalline solids, *Acta Metallurgica* 33, 331-357 (1985).
- P.W. Voorhees and W.C. Johnson, The thermodynamics of elastically stressed crystals, *Solid State Physics* 59, 1-201 (2004).

However, for most metallic solutions, diffusion is coupled with inelastic deformation, so that the theory of diffusion in elastic crystals is not applicable. See discussions in

- Z. Suo, A continuum theory that couples creep and self-diffusion. *Journal of Applied Mechanics* 71, 646-651 (2004). (<http://www.deas.harvard.edu/suo/papers/156.pdf>)

Equilibrium between a gel, a weight, and a pump. The theory coupling elastic network and mobile molecules has caused a great deal of confusion. It might be helpful if we start with elementary ideas.

A piece of hydrogel is subject to a force P , which may be applied by hanging a weight to the gel. The weight moves by displacement l . We will use the word weight as shorthand for any means to apply a mechanical force.

The gel also imbibes water from a pump. The chemical potential of water in the pump is μ , which can be varied by changing the pressure in the pump. See notes on chemical potential (<http://imechanica.org/node/911>). We assume that the gel can only imbibe water from the pump. Let N be the number of water molecules in the gel. We will use the word pump as shorthand for any means to supply water molecules. For example, the gel can be immersed in pure liquid water, or in a moist environment, or in a glass of wine. In the last case, the gel and the wine is separated by a semi-impermeable membrane, such that only water molecules can go through, but not any other species of molecules.

Furthermore, the gel is in contact with a reservoir of energy, which fixes the temperature of the gel. We will study isothermal changes, and will drop the dependence on temperature.

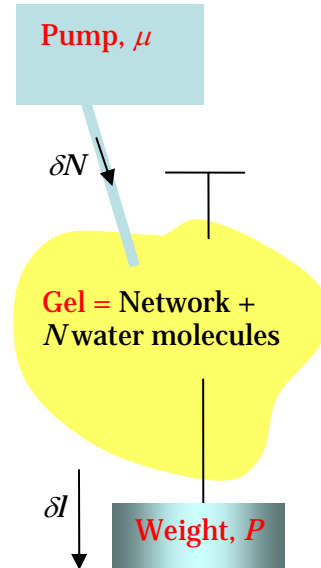
When the force P or the chemical potential μ change to a new set of values, the weight will move, the gel will imbibe water from the pump, and water will migrate in the gel. All these processes take time. So long as P and μ are fixed at this set of values, after some time, the gel will equilibrate with the weight and the pump. When this equilibrium is attained, how much distance does the weight move, and how much water does the pump inject?

To fix ideas, let us consider the following scenario. Between the pump and the gel is a valve, which controls the rate of injection. After flowing through the valve, water will then migrate in the gel. We assume that the injection is slow enough to allow water to redistribute in the gel, so that the gel by itself is in equilibrium.

Under the isothermal conditions, the thermodynamics of the gel is characterized by the Helmholtz free energy F as a function of two variables: the displacement of the weight, l , and the number of water molecules imbibed from the pump, N , namely,

$$F = F(l, N).$$

Associated with the small changes δl and δN , the free energy of the gel increases by



$$\delta F = \frac{\partial F(I, N)}{\partial I} \delta I + \frac{\partial F(I, N)}{\partial N} \delta N.$$

Upon moving by a small displacement δI , the weight does work $P\delta I$. Upon injecting into the gel a small number of water molecules, δN , the pump does work $\mu\delta N$.

When the gel equilibrates with the weight and the pump, the change in the free energy of the gel equals the sum of the work done by the weight and the work done by the pump, namely,

$$\delta F = P\delta I + \mu\delta N.$$

Combining this condition of equilibrium with the differential form of the free-energy function, we obtain that

$$\left[\frac{\partial F(I, N)}{\partial I} - P \right] \delta I + \left[\frac{\partial F(I, N)}{\partial N} - \mu \right] \delta N = 0.$$

Because I and N are independent variables, this condition of equilibrium requires the two separate equations:

$$P = \frac{\partial F(I, N)}{\partial I},$$

$$\mu = \frac{\partial F(I, N)}{\partial N}.$$

Let us reiterate the significance of the second condition. The left-hand side of the equation is the chemical potential of water in the pump, and the right-hand side of the equation is the chemical potential of water in the gel. When the pump and the gel equilibrate, the chemical potential of water is the same in the pump and in the gel.

The free-energy function $F(I, N)$ is taken to be known. Once P is set by the weight, and μ set by the pump, the above conditions of equilibrium are a pair of simultaneous nonlinear algebraic equations that determine I and N when the gel equilibrates with the weight and the pump.

Experimental determination of the function $F(I, N)$. The function $F(I, N)$ can be determined by the condition of equilibrium:

$$\delta F = P\delta I + \mu\delta N.$$

The four quantities on the right-hand side of the equation can all be determined by experiments. Given a gel, we can gradually vary P and μ by adjusting the weight and the pump. For each small change in P and μ , we wait long enough for the gel to equilibrate with the new levels of P and μ , and then measure the changes δI and δN in equilibrium. An integration of the above equation gives the function $F(I, N)$.

Chemical potential as an independent variable. When the gel equilibrates with the weight and the pump, the chemical potential of water in the pump equals the chemical potential of water in the gel, namely,

$$\mu = \frac{\partial F(I, N)}{\partial N}.$$

Given the function $F(I, N)$ and the chemical potential μ , the above equation is a nonlinear algebraic equation, from which we can solve N in terms of I and μ . We may wish to use I and μ as independent variables.

Define a new quantity

$$\hat{F} = F - \mu N,$$

Combining this definition with the condition of equilibrium,

$$\delta F = P\delta I + \mu\delta N,$$

we obtain that

$$\delta \hat{F} = P\delta I - N\delta \mu.$$

Consequently, once we express \hat{F} as a function of I and μ , namely,

$$\hat{F} = \hat{F}(I, \mu),$$

the partial derivatives are interpreted as

$$P = \frac{\partial \hat{F}(I, \mu)}{\partial I}, \quad -N = \frac{\partial \hat{F}(I, \mu)}{\partial \mu}.$$

These equations are yet another equivalent representation of the conditions of equilibrium between the gel, the weight, and the pump.

A gel couples chemistry and mechanics. A change of the chemical potential of water in the pump will cause the gel to swell or contract, displacing the weight. Conversely, a change of the weight will also cause the gel to swell or contract, which will in turn change the number of water molecules in the gel. This two-way coupling is the basis for the gel to be used as actuators and sensors.

When the gel equilibrates with the weight and the pump, the four types of small changes are related through the Hessian of the free energy function:

$$\begin{aligned} \delta P &= \frac{\partial^2 F(I, N)}{\partial I^2} \delta I + \frac{\partial^2 F(I, N)}{\partial I \partial N} \delta N, \\ \delta \mu &= \frac{\partial^2 F(I, N)}{\partial N \partial I} \delta I + \frac{\partial^2 F(I, N)}{\partial N^2} \delta N. \end{aligned}$$

Just like thermal expansion of a material may be used to measure the temperature, moisture-induced deformation of a gel can be used to measure the chemical potential of water.

Exercise: stability of the state of equilibrium against small perturbation. A gel is characterized by a Helmholtz free energy $F(I, N)$. After the gel is connected to a weight and a pump for a long time, the gel equilibrates with the weight and the pump. Given the force due to the weight, P , and the

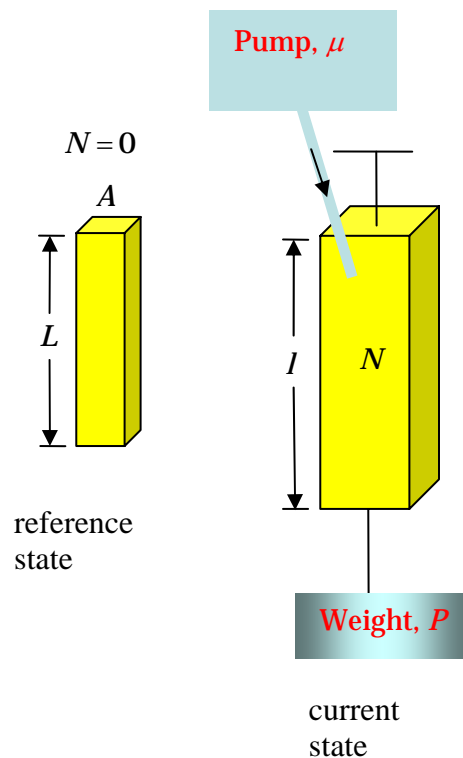
chemical potential of water in the pump, μ , the above theory determines the values of l and N when the gel equilibrates with the weight and the pump. Derive the condition under which this state of equilibrium is stable against arbitrary small changes in l and N .

The need for a field theory of inhomogeneous deformation. So far as the above theory is concerned, there is nothing special about the gel or water. The theory is applicable to any elastic solid and any mobile species. The theory is applicable when the gel is a molecule, a cell, or a tissue.

We next formulate a field theory. When the weight and the chemical potential of water in the pump change, water molecules must diffuse in or out of the gel. We would like to describe this nonequilibrium process. If the gel is homogeneous over a size scale of interest to us, we can benefit from a field theory. The associated boundary and initial value problems will allow us to study inhomogeneous deformation of the network and inhomogeneous distribution of water molecules. The theory will also enable us to calculate the time needed for the gel to settle to a new state of equilibrium after a load is applied.

To formulate a field theory for inhomogeneous deformation, we will model a gel by a field of material particles. Each material particle undergoes homogeneous deformation. Furthermore, each material particle is capable of imbibing water.

Equilibrium between a rod, a weight, and a pump. As a preparation for a more general theory, consider a rod of a gel in a state of homogeneous swelling. Any state may be used as a reference state. For example, we will use the dry network as the reference state, in which there is no water molecules, $N = 0$. In the reference state, the rod has a cross-sectional area A and length L . Subsequently, a weight applies to the gel a force P , and a pump injects into the gel water at the chemical potential μ . When the gel equilibrates with the weight and the pump, the network is in a homogenous state of deformation. We designate this state of equilibrium as the current state, where the length of the rod becomes l , and the number of water molecules in the gel is N .



Let $F(l, N)$ be the free energy of the rod. When the rod equilibrates with the weight and the pump, the change in the free energy of the rod equals the sum of the work done by the weight and by the pump:

$$\delta F = P\delta l + \mu\delta N.$$

Divide this equation by the volume in the reference state, $V = AL$, we obtain that

$$\delta W = s\delta\lambda + \mu\delta C.$$

In writing this equation, we have defined the nominal density of free energy

$$W = \frac{F}{V},$$

the stretch

$$\lambda = \frac{l}{L},$$

the nominal stress

$$s = \frac{P}{A},$$

and the nominal concentration

$$C = \frac{N}{V}.$$

We have chosen to use the length, area and volume of the rod in the reference state to normalize the quantities in the current state.

As a material model, we specify the nominal density of free energy as a function of the stretch of the network and the concentration of water:

$$W = W(\lambda, C).$$

The differential of the function is

$$\delta W = \frac{\partial W(\lambda, C)}{\partial \lambda} \delta\lambda + \frac{\partial W(\lambda, C)}{\partial C} \delta C.$$

When the rod is in equilibrium with the weight and the pump, $\delta W = s\delta\lambda + \mu\delta C$.

A comparison of the two equations gives

$$s = \frac{\partial W(\lambda, C)}{\partial \lambda}, \quad \mu = \frac{\partial W(\lambda, C)}{\partial C}.$$

These equations are the conditions of equilibrium between the gel, the weight, and the pump.

Chemical potential as an independent variable. We can also use the chemical potential as an independent variable. Define a new function

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

Combining this equation with the condition of equilibrium,

$$\delta W = s\delta\lambda + \mu\delta C,$$

we obtain that

$$\delta \hat{W} = s\delta\lambda - C\delta\mu.$$

The new free energy is a function of the stretch and chemical potential, namely,

$$\hat{W} = \hat{W}(\lambda, \mu)$$

The stress and the concentrations are given by

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

These equations are yet another representation of the conditions of equilibrium between the rod, the weight, and the pump.

Inhomogeneous deformation of a gel in equilibrium with weights and pumps. 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,

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

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.

Summary of equations. We may as well identify the nominal stress and chemical potential with the differential coefficients of the free energy function:

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

The conditions for mechanical equilibrium become

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

in the volume, and

$$s_{iK} N_K = T_i$$

on the surface.

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 Legendre 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

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

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

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

Finite element method to study large inhomogeneous deformation in gels. Let us summarize the basic equations. 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 condition of equilibrium is 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 .

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 a hyperelastic body. A finite element method has been implemented in ABAQUS by Hong, Liu and Suo (IJSS, in press, 2009). The preprint of the paper, along with 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.

The next few paragraphs collect ideas on constructing material models.

Invariance under rigid-body rotation. To ensure that W is invariant under rigid-body rotation, we invoke the Lagrange strain

$$L_{KM} = \frac{1}{2}(F_{iK}F_{iM} - \delta_{KM}),$$

which is invariant when the entire system in the current state undergoes a rigid-body rotation. Consequently, a conservative dielectric is characterized by the energy function $W(\mathbf{L}, C)$. The nominal stress and the nominal electric field are obtained from partial derivatives:

$$s_{iK}(\mathbf{L}, C) = F_{iM} \frac{\partial W(\mathbf{L}, C)}{\partial L_{KM}}, \quad \mu(\mathbf{L}, C) = \frac{\partial W(\mathbf{L}, C)}{\partial C}.$$

Isotropic material. For an isotropic material, a reference state exists such that the energy density is a function of the invariants formed by the tensor \mathbf{L} and the scalar C :

$$L_{KK}, L_{KN}L_{KN}, L_{KN}L_{NM}L_{MK}, C.$$

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.

Superposing models of elasticity and models of solution. When the polymers are not crosslinked, individual polymeric molecules may dissolve in a solvent (e.g., water). A large number of models of solutions exist. When the polymers are crosslinked, the network acquires entropic elasticity. A large number of models of solution exist.

In many gels, the density of the crosslinks is very low, such as one crosslink per 1000 monomers. Consequently, to the first approximation, we may neglect the coupling effect of the crosslinks on solution, and simply write the free energy of the gel as the sum of the free energy of the network and the free energy of the solution.

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 of a gel comes from two molecular processes: stretching the network of the polymers, and mixing the polymers and the small molecules. Write the free energy of the gel as a sum:

$$W(\mathbf{F}, C) = W_{stretch}(\mathbf{F}) + W_{mix}(C),$$

where $W_{stretch}$ and W_{mix} are the contributions from stretching and mixing, respectively.

Let λ_1 , λ_2 and λ_3 be the three stretches. The free energy due to stretching a network of polymers is taken to be

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

where M 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 $\chi > 0$.

Stress-stretch relations under the condition of molecular incompressibility. We assume molecular incompressibility, namely,

$$vC + 1 = \lambda_1 \lambda_2 \lambda_3.$$

Consequently, the nominal density of free energy is a function of only three independent variables:

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

When the stretches vary by small amounts, the free energy varies by

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

Consider a block of a gel subject to forces in three directions, and a pump which injects water at chemical potential μ . Let s_1 , s_2 and s_3 be the three nominal stresses associated with the applied forces. When the gel equilibrates with the forces and the pump, the change in the free energy equals the work done by the forces and the pump, namely,

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

Inserting the condition of molecular incompressibility, $vC + 1 = \lambda_1 \lambda_2 \lambda_3$, we obtain that

$$\delta W = \left(s_1 + \frac{\mu}{v} \lambda_2 \lambda_3 \right) \delta \lambda_1 + \left(s_2 + \frac{\mu}{v} \lambda_1 \lambda_2 \right) \delta \lambda_2 + \left(s_3 + \frac{\mu}{v} \lambda_1 \lambda_2 \right) \delta \lambda_3.$$

Because the three stretches can vary independently, a comparison of the two sides of equation gives

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

Recall that the nominal stresses relate to the true stresses as

$$s_1 = \sigma_1 \lambda_2 \lambda_3, \quad s_2 = \sigma_2 \lambda_3 \lambda_1, \quad s_3 = \sigma_3 \lambda_1 \lambda_2.$$

Consequently, in terms of the true stresses, the above equations become

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

Thus, an increase in the chemical potential of water in the pump will superimpose a hydrostatic pressure to the gel.

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

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

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,

where the chemical potential of the solvent can be varied by adjusting the pump. The term scaling with MkT 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 .

Is osmotic pressure a valid idea for gels? Osmotic pressure is a measurable quantity in a liquid solution, but is not 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 the stretching of the network.

In a liquid solution, osmosis occurs when is 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 specific 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.

Diffusion in a rigid network. We now review diffusion of a species of molecules through a rigid network. We name a material particle in the network

by the coordinate of the particle, \mathbf{X} . Consider a block of the network around \mathbf{X} , of volume $dV(\mathbf{X})$. The network may contain interfaces between dissimilar parts. Let $N_\kappa(\mathbf{X})dA(\mathbf{X})$ be an area element of an interface, where $dA(\mathbf{X})$ is the area of the element, and $N_\kappa(\mathbf{X})$ is the unit vector normal to the element.

The number of molecules is conserved. Imagine a field of pumps attached to the network, injecting molecules into the network. Let the number of the molecules injected into a volume element be $r(\mathbf{X}, t)dV(\mathbf{X})$, and into an element of surface be $j(\mathbf{X}, t)dA(\mathbf{X})$. The molecules also diffuse in the network. Let $J_\kappa(\mathbf{X}, t)$ be the flux of the molecules, namely, the number molecules per unit time crossing per unit area in direction X_κ . We assume that no chemical reaction occurs, so that the number of the molecules is conserved, namely,

$$\frac{\partial C(\mathbf{X}, t)}{\partial t} + \frac{\partial J_\kappa(\mathbf{X}, t)}{\partial X_\kappa} = r(\mathbf{X}, t)$$

in the volume, and

$$J_\kappa(\mathbf{X}, t)N_\kappa(\mathbf{X}, t) = -j(\mathbf{X}, t).$$

on an interface.

Fick's law. The diffusion flux is taken to be proportional to the concentration gradient:

$$J_\kappa(\mathbf{X}, t) = D \frac{\partial C(\mathbf{X}, t)}{\partial X_\kappa}.$$

The coefficient of diffusion, D , is often taken to be constant.

The conservation of molecules and Fick's law together provide a complete set of PDEs. For many problems, one can set $r = 0$. A combination of the above gives the well known diffusion equation:

$$\frac{\partial C(\mathbf{X}, t)}{\partial t} = D \frac{\partial^2 C(\mathbf{X}, t)}{\partial X_\kappa \partial X_\kappa}.$$

On the boundary of the network, one needs to prescribe boundary conditions. Examples include

- Prescribe flux j . For example, when the network is sealed, no molecules can enter or escape.
- Prescribe concentration C . If molecules can enter, or escape from, the body, diffusion inside the network may take much longer time than the process on the surface, so that the molecules are in local equilibrium at the surface. That is, the chemical potential of the molecules in the environment is the same as the chemical potential of the molecules in the network near the surface. The former is taken to be given, and the latter is a function of the concentration. Another way to say this is that the concentration on the surface equals the solubility in equilibrium with the environment.
- Prescribe reaction kinetics. If the process of molecules entering or escaping is slow, the chemical potential of the molecules in the solid near the surface may be different from the chemical potential in the

environment. The difference drives the process of entering or escaping. One can prescribe the reaction kinetics by giving a relation between j and the difference in the chemical potentials.

The diffusion equation is linear. Dimensional analysis shows that, for an event on a length scale L to occur, the time scale is

$$\tau = \frac{L^2}{D}.$$

This is the single most significant result in the theory of diffusion. Much of the qualitative understanding of phenomena revolves around this result, and requires no detailed solution of the initial and boundary value problems.

You can, however, find solutions for many boundary and initial value problems in textbooks. Here are a few good ones:

- E.L. Cussler, Diffusion, 2nd edition. Cambridge University Press, 1997.
- J. Crank, The mathematics of diffusion, 2nd edition, Clarendon Press, Oxford, 1994.
- H.S. Carslaw and J.C. Jaeger, Conduction of heat in solids, Clarendon Press, Oxford, 1959.
- M.E. Glicksman, Diffusion in solids, John Wiley, 2000.

Fluid infiltrating a rigid network. When the pores in a network are much larger than the molecular dimension, the migration of molecules in the network may as well be thought of fluid flowing in a pipe, driven by the gradient in the pressure.

Darcy's law. The flux of fluid is proportional to the pressure gradient:

$$J_\kappa = -\frac{\kappa}{v\eta} \frac{\partial p(\mathbf{X}, t)}{\partial X_\kappa},$$

where $p(\mathbf{X}, t)$ is the pressure in the fluid, η the viscosity of the fluid, v is the volume per molecule, and κ has the dimension of length squared. κ depends on the size and arrangement of the pores, but is independent of the fluid.

The fluid is taken to be compressible. Let the concentration and the pressure be related by a thermodynamic function $C = C(p)$, so that

$$\frac{\partial C(\mathbf{X}, t)}{\partial t} = \frac{dC(p)}{dp} \frac{\partial p(\mathbf{X}, t)}{\partial t}.$$

A combination of the conservation of molecules, Darcy's law, and compressibility gives

$$\frac{\partial p(\mathbf{X}, t)}{\partial t} = \left(\frac{dC(p)}{dp} \right)^{-1} \frac{\kappa}{v\eta} \frac{\partial^2 p(\mathbf{X}, t)}{\partial X_\kappa \partial X_\kappa}.$$

The pre-factor is often taken to be a constant, so that the equation looks the same as the diffusion equation. The solutions will also be similar to those of the diffusion equation.

Thermodynamics of irreversible processes (TIP). The above theories seem somewhat *ad hoc*. A more potent recipe to construct such theories is the thermodynamics of nonequilibrium process.

The fluid-infiltrated network is characterized by a free energy function $W(C)$. The rate of change in the free energy of the gel is

$$\begin{aligned} \int \frac{\delta W}{\delta t} dV &= \int \frac{\partial W}{\partial C} \frac{\partial C(\mathbf{X}, t)}{\partial t} dV = - \int \frac{\partial W}{\partial C} \frac{\partial J_\kappa}{\partial X_\kappa} dV + \int \frac{\partial W}{\partial C} r dV \\ &= \int J_\kappa \frac{\partial}{\partial X_\kappa} \left(\frac{\partial W}{\partial C} \right) dV - \int \frac{\partial}{\partial X_\kappa} \left(\frac{\partial W}{\partial C} J_\kappa \right) dV + \int \frac{\partial W}{\partial C} r dV \quad . \\ &= \int J_\kappa \frac{\partial}{\partial X_\kappa} \left(\frac{\partial W}{\partial C} \right) dV + \int \frac{\partial W}{\partial C} j dA + \int \frac{\partial W}{\partial C} r dV \end{aligned}$$

We have used the conservation of molecules and the divergence theorem.

Imagine a field of pumps attached to the network, injecting a species of molecules into the body. Let $\mu(\mathbf{X}, t)$ be the chemical potential at which the molecules are injected. Thermodynamics dictates that the rate of change in the free energy of the gel should not exceed the power delivered by the pumps, namely,

$$\int \frac{\delta W}{\delta t} dV \leq \int \mu r dV + \int \mu j dA .$$

A combination of the above two expressions give

$$\int J_\kappa \frac{\partial}{\partial X_\kappa} \left(\frac{\partial W}{\partial C} \right) dV + \int \left(\frac{\partial W}{\partial C} - \mu \right) r dV + \int \left(\frac{\partial W}{\partial C} - \mu \right) j dA \leq 0 .$$

This inequality must hold for any arbitrary fluxes r , j and J_κ . We will assume local equilibrium, so that the last two terms vanish, namely,

$$\mu = \frac{\partial W(C)}{\partial C} .$$

To ensure the above inequality for any diffuse flux, we need to ensure that the first term be negative. One common way to do this is to adopt a kinetic law

$$J_\kappa(\mathbf{X}, t) = -M \frac{\partial \mu(\mathbf{X}, t)}{\partial X_\kappa}$$

where M is a positive quantity, known as the mobility.

This kinetic law includes both Fick's law and Darcy's law as special cases. When the solution is an ideal solution, the chemical potential is

$$\mu(C) = \mu(C_0) + kT \log(C / C_0) .$$

Inserting this expression into the above kinetic law, we obtain that

$$J_\kappa(\mathbf{X}, t) = - \frac{kTM}{C} \frac{\partial C(\mathbf{X}, t)}{\partial X_\kappa} .$$

A comparison with Fick's law gives that

$$M = \frac{CD}{kT} .$$

This is Einstein's relation.

When the solvent is an incompressible fluid, the chemical potential is

$$\mu = \nu p.$$

Inserting this expression into the kinetic law, we obtain that

$$J_\kappa(\mathbf{X}, t) = -M\nu \frac{\partial p(\mathbf{X}, t)}{\partial X_\kappa}.$$

A comparison with Darcy's law gives that

$$M = \frac{\kappa}{\eta\nu^2}.$$

- I. Prigogine, Introduction to thermodynamics of irreversible processes. Wiley, New York.
- S.R. de Groot and P. Mazur, Non-equilibrium thermodynamics, Dover reprint, 1984.
- B.D. Coleman and W. Noll, The thermodynamics of elastic materials with heat conduction and viscosity. The Archive for Rational Mechanics and Analysis 13, 167-178 (1963).

Nonlinear poroelasticity. Let W be the free energy in a block in the current state divided by the volume of the block in the reference state. The free energy is taken to be a function of the deformation gradient and the concentration, $W(\mathbf{F}, C)$. Associated with any virtual changes, $\delta F_{i\kappa}$ and δC , the free energy of the material element of volume changes by

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

Thermodynamics dictates that the rate of change in the free energy of the gel should not exceed the power delivered by the weights and the pumps, namely,

$$\int \frac{\delta W}{\delta t} dV \leq \int B_i \frac{\delta x_i}{\delta t} dV + \int T_i \frac{\delta x_i}{\delta t} dA + \int \mu r dV + \int \mu j dA.$$

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

$$\begin{aligned} & \int \left[\frac{\partial W}{\partial F_{i\kappa}} N_\kappa - T_i \right] \frac{\delta x_i}{\delta t} dA - \int \left[\frac{\partial}{\partial X_\kappa} \left(\frac{\partial W}{\partial F_{i\kappa}} \right) + B_i \right] \frac{\delta x_i}{\delta t} dV \\ & + \int \left(\frac{\partial W}{\partial C} - \mu \right) j dA + \int \left(\frac{\partial W}{\partial C} - \mu \right) r dV \\ & + \int J_\kappa \frac{\partial}{\partial X_\kappa} \left(\frac{\partial W}{\partial C} \right) dV \leq 0 \end{aligned}$$

This inequality must hold for any arbitrary r, j and $J_\kappa, \delta x_i / \delta t$. We will assume local equilibrium, so that the first four terms vanish:

$$\frac{\partial s_{iK}(\mathbf{X}, t)}{\partial X_K} + B_i(\mathbf{X}, t) = 0$$

in volume,

$$s_{iK} N_K = T_i$$

on an interface, and

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

To ensure the above inequality for any diffuse flux, we need to ensure that the first term be negative. One common way to do this is to adopt a kinetic law

$$J_K(\mathbf{X}, t) = -M \frac{\partial \mu(\mathbf{X}, t)}{\partial X_K},$$

where M is the positive number, known as the mobility.

Summary of equations. The theory evolves the deformation of the network, $x_i(\mathbf{X}, t)$, and the concentration of the solvent, $C(\mathbf{X}, t)$. Other choices of basic fields are possible.

$$\text{Deformation gradient: } F_{iK}(\mathbf{X}, t) = \frac{\partial x_i(\mathbf{X}, t)}{\partial X_K}$$

Conservation of molecules:

$$\frac{\partial C(\mathbf{X}, t)}{\partial t} + \frac{\partial J_K(\mathbf{X}, t)}{\partial X_K} = r(\mathbf{X}, t)$$

in the volume of the network, and

$$J_K N_K(\mathbf{X}, t) = -j(\mathbf{X}, t),$$

on an interface.

Conservation of momentum:

$$\frac{\partial s_{iK}(\mathbf{X}, t)}{\partial X_K} + B_i(\mathbf{X}, t) = 0$$

in the volume of the body, and

$$s_{iK} N_K = T_i$$

on an interface.

$$\text{Local equilibrium: } s_{iK} = \frac{\partial \hat{W}(\mathbf{F}, \mu)}{\partial F_{iK}}, \quad C = -\frac{\partial \hat{W}(\mathbf{F}, \mu)}{\partial \mu}.$$

$$\text{Kinetic model: } J_K(\mathbf{X}, t) = -M(\mathbf{F}, \mu) \frac{\partial \mu(\mathbf{X}, t)}{\partial X_K}.$$

The above theory evolves the configuration of the gel, namely, evolves concurrently the two fields $\mathbf{x}(\mathbf{X}, t)$ and $\mu(\mathbf{X}, t)$, once the following items are prescribed:

- the initial conditions $\mathbf{x}(\mathbf{X}, t_0)$ and $\mu(\mathbf{X}, t_0)$ at a particular time t_0
- the applied force $B_i(\mathbf{X}, t)$ and the rate of injection $r(\mathbf{X}, t)$ inside the gel
- either $j(\mathbf{X}, t)$ or $\mu(\mathbf{X}, t)$ on the surface of the gel
- either $T_i(\mathbf{X}, t)$ or $\mathbf{x}(\mathbf{X}, t)$ on the surface of the gel
- the free-energy function $\hat{W}(\mathbf{F}, \mu)$ and the mobility tensor $M_{KL}(\mathbf{F}, \mu)$.

Opportunities to study transient processes in gels. A large body of literature exists on linear poroelasticity. By contrast, the literature on nonlinear poroelasticity is limited. Opportunities for study include

- Develop models for the mobility tensor when the network undergoes large deformation.
- Develop finite element method to analyze transient processes in gels undergoing large deformation. See a review of the literature in <http://imechanica.org/node/3895>.
- Apply the theory to important phenomena.

Linear poroelasticity. If disturbance from the reference state is small, we may approximate material models by linear relations. For example, set the reference state to be a rod subject to no weight but is subject to 100% relative humidity. The chemical potential and the water concentration are measured relative to the reference state. We will also use the engineering strain e , instead of the stretch, to represent the deformation. Assume that the function $\tilde{W}(\sigma, \mu)$ is a quadratic form:

$$\tilde{W}(\sigma, \mu) = -\frac{\sigma^2}{2E} - \alpha\sigma\mu - \frac{\beta\mu^2}{2},$$

Where E , α and β are material constants. Thus,

$$e = \frac{\sigma}{E} + \alpha\mu$$

$$C = \alpha\sigma + \beta\mu$$

The coefficient α behaves like the coefficient of thermal expansion, and gives the strain associated with unit change in the chemical potential. Indeed, if we take the unit of temperature and that of chemical potential both as the unit of energy, the coefficient α will have the same unit as that of coefficient of thermal expansion.

The three material constants form a dimensionless parameter

$$\xi = \alpha \sqrt{\frac{E}{\beta}}.$$

This parameter measures the significance of the interaction between elasticity and chemistry.

Generalizing to a state of multiaxial stress is straightforward:

$$\begin{aligned}\tilde{W}(\sigma, \mu) &= -\frac{1}{2} S_{ijkl} \sigma_{ij} \sigma_{kl} - \alpha_{kl} \sigma_{kl} \mu - \frac{1}{2} \beta \mu^2. \\ e_{ij} &= S_{ijkl} \sigma_{kl} + \alpha_{ij} \mu \\ C &= \alpha_{ij} \sigma_{ij} + \beta \mu\end{aligned}$$

An isotropic, linearly poroelastic material is characterized by a total of 4 independent material constants:

- 2 for the tensor S_{ijkl} ,
- 1 for the tensor α_{ik} , and
- 1 constant β .

The thermodynamic model is written as

$$\begin{aligned}e_{ij} &= \frac{(1+\nu)}{E} \sigma_{ij} - \frac{\nu}{E} \sigma_{kk} \delta_{ij} + \alpha \mu \delta_{ij} \\ C &= \alpha \sigma_{kk} + \beta \mu\end{aligned}$$

or more explicitly as

$$\begin{aligned}e_x &= \frac{1}{E} (\sigma_x - \nu \sigma_y - \nu \sigma_z) + \alpha \mu \\ e_y &= \frac{1}{E} (\sigma_y - \nu \sigma_x - \nu \sigma_z) + \alpha \mu \\ e_z &= \frac{1}{E} (\sigma_z - \nu \sigma_x - \nu \sigma_y) + \alpha \mu \\ e_{yz} &= \frac{1+\nu}{E} \sigma_{yz} \\ e_{zx} &= \frac{1+\nu}{E} \sigma_{zx} \\ e_{xy} &= \frac{1+\nu}{E} \sigma_{xy} \\ C &= \alpha (\sigma_x + \sigma_y + \sigma_z) + \beta \mu\end{aligned}$$

There are many ways to regroup these four material constants.

When deformation is small, we may disregard the difference between the reference and the current state in writing equilibrium equations. Let σ_{ij} be the stress, and write the force balance in the usual way:

$$\frac{\partial \sigma_{ij}}{\partial x_j} = 0 \quad \text{in volume}$$

$$\sigma_{ij} n_j = t_i \quad \text{on surface.}$$

We will adopt the linearized displacement-strain relations

$$e_{ij} = \frac{1}{2} \left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right).$$

The kinetic law takes the form

$$J_i = -M \frac{\partial \mu}{\partial x_i}.$$

The conservation of molecules takes the form

$$\frac{\partial C}{\partial t} + \frac{\partial J_i}{\partial x_i} = 0.$$

For an event to occur over time scale L , the time needed scales as

$$\tau = \frac{\beta}{M} L^2.$$

Linear poroelasticity has been implemented in ABAQUS. In what followings we describe several boundary-value problems to illustrate basic behaviors.

Stress in a thin film due to change of the humidity in the environment. A porous film can absorb water in a moist environment. The film may develop a biaxial stress. Because the in-plane strain is constrained by the substrate, which does not absorb water, so that the in plane strain vanishes:

$$0 = \frac{1-\nu}{E} \sigma + \alpha \mu,$$

Thus, the biaxial stress is

$$\sigma = -\frac{E\alpha\mu}{1-\nu}.$$

The concentration of water changes by

$$C = 2\alpha\sigma + \beta\mu = \left(-\frac{2E\alpha^2}{1-\nu} + \beta \right) \mu.$$

Stress in a body induced by drying. A large body is in equilibrium with moisture of a certain chemical potential. When the chemical potential is suddenly changed, the bulk of the body do not change dimension rapidly, but the surface layer will change moisture content. Let the change in the chemical potential in the moisture be μ_0 . The chemical potential of water in the body is a time-dependent field, $\mu(z, t)$. We assume local equilibrium,

$$\mu(0, t) = \mu_0.$$

In the interior of the body, far beneath the surface, the chemical potential remains unchanged, namely

$$\mu(\infty, t) = 0.$$

These two equations set the boundary conditions for the field of chemical potential.

The body is in a state of equal biaxial stress, $\sigma(z, t)$. The lateral strain everywhere is zero,

$$0 = e_x = \frac{1-\nu}{E} \sigma + \alpha \mu,$$

so that

$$\sigma = -\frac{E\alpha}{1-\nu} \mu.$$

The concentration is

$$C = 2\alpha\sigma + \beta\mu = \bar{\beta}\mu,$$

with

$$\bar{\beta} = \beta - \frac{2E\alpha^2}{1-\nu}$$

Inserting this relation into

$$J = -M \frac{\partial \mu}{\partial z}, \quad \frac{\partial C}{\partial t} + \frac{\partial J}{\partial z} = 0,$$

And we obtain that

$$\frac{\partial \mu}{\partial t} = \frac{M}{\bar{\beta}} \frac{\partial^2 \mu}{\partial z^2}.$$

This PDE, together with the initial and boundary conditions, yields the distribution of the chemical potential:

$$\mu(z, t) = \mu_0 (1 - \text{erf} \zeta),$$

$$\text{erf} \zeta = \frac{2}{\sqrt{\pi}} \int_0^{\zeta} \exp(-s^2) ds,$$

$$\zeta = \frac{z}{2\sqrt{tM/\bar{\beta}}}.$$

The distribution of stress is similar.

A test for soils (Biot, 1941). A column of soil, height h , is saturated with water, and is under no applied forces at time $t < 0$. At time zero, a stress $\sigma_z = \sigma_0$ is applied to the top surface of the soil, and this stress is applied in the subsequent time. The column is confined laterally in a rigid sheath so that no lateral expansion can occur. There is no friction between the column and the sheath. Also, no water can escape laterally or through the bottom, while water is free to escape at the top surface by applying the load through a very porous slab. These idealizations ensure that the soil undergoes uniaxial deformation. The state of stress, however, is triaxial.

The state of equilibrium. After some time, the column equilibrates with the load. In this state of equilibrium, the chemical potential of water in the column is homogeneous and equals that of the environment, which is taken to be the reference, namely, $\mu = 0$ in liquid water under no pressure. In equilibrium,

the solid will be in a state of uniform triaxial stress:

$$\sigma_z = \sigma_0, \quad \sigma_x = \sigma_y.$$

The lateral confining stress is determined by setting the lateral strain to be zero:

$$0 = e_x = \frac{1-\nu}{E} \sigma_x - \frac{\nu}{E} \sigma_0$$

so that

$$\sigma_x = \sigma_y = \frac{\nu}{1-\nu} \sigma_0.$$

The change in the concentration of water in the soil is

$$C_{eq} = \alpha \sigma_{kk} = \frac{1+\nu}{1-\nu} \alpha \sigma_0.$$

If the applied load is compressive, when the soil equilibrates with the compression, the total number of water molecules escaped from the soil is C_{eq} times the volume of the column.

The process to attain the state of equilibrium. From dimensional analysis, we already know the time scale to reach equilibrium scales as

$$\tau = h^2 \beta / M.$$

We can easily sketch the trend of the behavior. Here we solve for the entire history of evolution.

Let us first list all the nonzero fields. The lateral displacements vanish at all times, but the vertical displacement is a time dependent field, $u_z(z, t)$. The only non-vanishing component of the strain tensor is $e_z(z, t)$. The chemical potential of water in the column is also a time-dependent field, $\mu(z, t)$, and so and the change in the concentration, $C(z, t)$, and the flux $J(z, t)$. By force balance, the vertical component of the stress tensor equal to the applied stress at all times:

$$\sigma_z(z, t) = \sigma_0.$$

The lateral components of the stress tensor are time-dependent fields. By symmetry the two fields are equal, namely,

$$\sigma_x(z, t) = \sigma_y(z, t).$$

We next list all the governing equations. The forces have already been balanced, so we do not list equations for force balance. The vertical strain relates to the vertical displacement by

$$e_z = \frac{\partial u_z(z, t)}{\partial z}.$$

The thermodynamic model is reduced to

$$e_x = \frac{1-\nu}{E} \sigma_x - \frac{\nu}{E} \sigma_0 + \alpha \mu$$

$$e_z = \frac{\sigma_0}{E} - \frac{2\nu}{E} \sigma_x + \alpha \mu$$

$$C = \alpha(2\sigma_x + \sigma_0) + \beta \mu.$$

The conservation of the number of water molecules requires that

$$\frac{\partial C}{\partial t} + \frac{\partial J}{\partial z} = 0.$$

The kinetic model is

$$J = -M \frac{\partial \mu}{\partial z}.$$

We next combine these equations into a single partial differential equation for $\mu(z, t)$.

Setting $e_x = 0$ in the thermodynamic model, we obtain that

$$\sigma_x = \frac{\nu}{1-\nu} \sigma_0 - \frac{E\alpha\mu}{1-\nu}.$$

In the transient process, the chemical potential of water in the soil deviates from the value of the pure liquid water, which is set to be zero. This nonzero chemical potential contributes to the stress in the transverse directions.

Inserting this expression for stress into the thermodynamic equation for C , we obtain that

$$C = \alpha \frac{1+\nu}{1-\nu} \sigma_0 + \bar{\beta} \mu,$$

with

$$\bar{\beta} = \beta - \frac{2E\alpha^2}{1-\nu}.$$

Thus, the nonzero chemical potential of water during the transient process also affects the water content in the soil.

A combination of the above equations gives the partial differential equation for $\mu(z, t)$:

$$\frac{\partial \mu}{\partial t} = \frac{M}{\bar{\beta}} \frac{\partial^2 \mu}{\partial z^2}.$$

This is the familiar diffusion equation subject to the following initial and boundary conditions.

At time $t=0$, the water content everywhere in the soil is still at the level of the saturated soil under no stress, which is taken to be the reference, $C(z,0)=0$. This gives the initial value of the chemical potential:

$$\mu(z,0) = -\left(\frac{1+\nu}{1-\nu}\right) \frac{\alpha}{\beta} \sigma_0$$

At the top of the column, $z=0$, the chemical potential in the soil is maintained by the environment, so that

$$\mu(0,t) = 0.$$

At the bottom of the column, $z=h$, water cannot escape, so that $J(h,t) = 0$, giving

$$\frac{\partial \mu}{\partial z}(h,t) = 0.$$

A separation of variable gives the form of the solution:

$$\mu(z, t) = \sum_n a_n \sin\left(\frac{2n-1}{2} \pi \frac{z}{h}\right) \exp\left[-\left(\frac{2n-1}{2} \pi\right)^2 \frac{t}{h^2 \beta / M}\right].$$

Inserting into the initial condition, we obtain the coefficients:

$$a_n = -\frac{(-1)^{n+1} 8}{(2n-1)^2 \pi^2} \left(\frac{1+\nu}{1-\nu}\right) \frac{\alpha}{\beta} \sigma_0.$$

From $\mu(z, t)$ we can obtain other fields.

Exercise. Determine the time-dependent field of the displacement. Plot your result.

A stationary long crack. The following two examples are analogous to those given in R. Huang, J.H. Prévost, Z. Suo, [Loss of constraint on fracture in thin film structures due to creep](#). Acta Materialia, 50, 4137-4148, 2002. Consider a long crack in a large body. When the body is equilibrated with the environment, the field chemical potential in the body is homogenous, and the body is stress-free. At time zero, the chemical potential of the environment is suddenly dropped by μ_0 . The migration of molecules along the crack is taken to be so fast that the the chemical potential in the crack also drops by μ_0 . As water molecules diffuse out from the body into the crack, a stress field develops inside the body. We would like to know the stress intensity factor of the crack.

Here we will only perform a scaling analysis. The drop in chemical potential set up a stress scale, $\sigma_0 = \mu_0 \alpha E$. At time t , diffusion of water molecules inside the body set up a length scale $\sqrt{tM/\beta}$. The stress intensity factor has the dimension $K = [\text{stress}][\text{length}]^{1/2}$. Consequently, the stress intensity factor takes the form

$$K = \kappa \mu_0 \alpha E (tM/\beta)^{1/4},$$

where κ is a dimensionless function of Poisson's ratio ν and the interaction parameter $\xi = \alpha \sqrt{E/\beta}$.

A crack extending at a constant velocity. Assume that a crack grows at a constant velocity. The stress intensity factor K and the stress level σ_0 form a length scale $(K/\sigma_0)^2$. Dimensional consideration gives the form of the velocity:

$$v = g \frac{M/\beta}{(K/\sigma_0)^2},$$

where g is a dimensionless function of Poisson's ratio ν and the interaction parameter $\xi = \alpha \sqrt{E/\beta}$.