Poroelasticity, or migration of matter 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 (1878) 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 describing 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.

Gibbs restricted himself to the state of equilibrium, and did not discuss the kinetic process of migration.

Consolidation of soils. The kinetic process of fluid migrating on an elastic host was considered by Biot (1941). 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

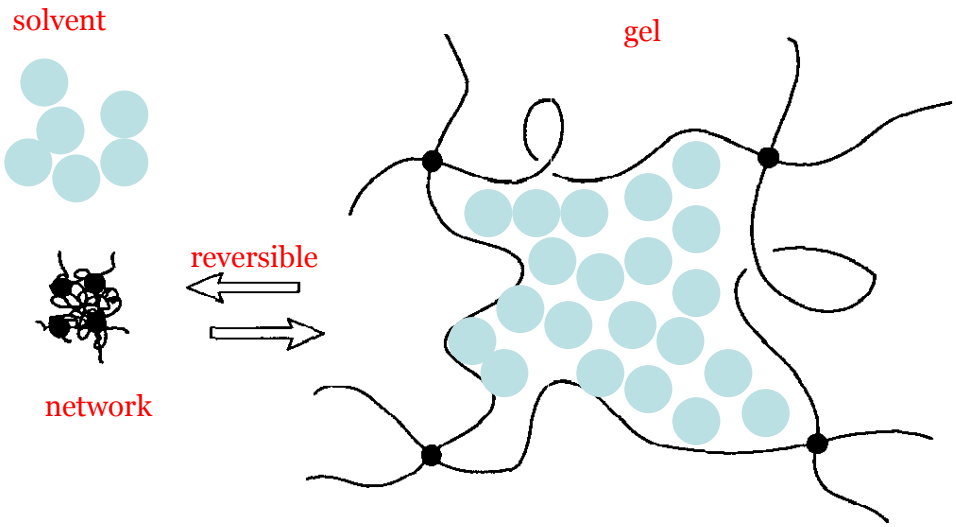
(http://esag.harvard.edu/rice/e2_Poroelasticity.pdf).

- 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).

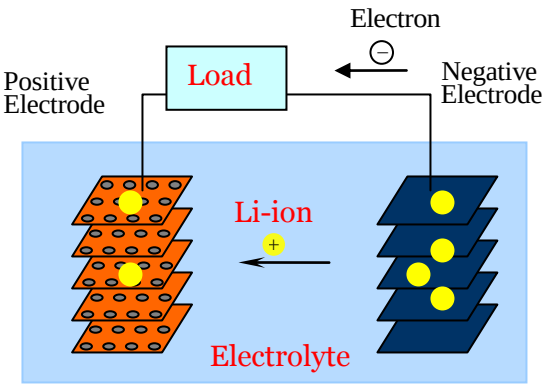


Tissues of animals and plants. Many tissues consist of elastic network and mobile molecules. The elasticity enables the tissues to retain shapes and deform, while mobile molecules enable the tissues to transport nutrients and wastes.

- 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 act9ive 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. Papers on the mechanics of lithium-ion battery have been appearing rapidly. Here are two examples.

- 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.

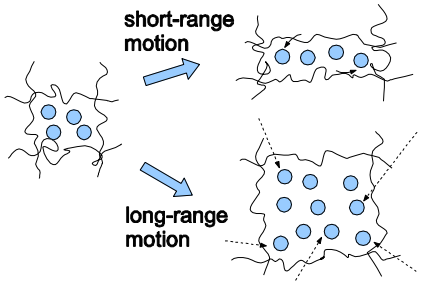
Diffusion in metallic solutions. In a metallic solution, one species of atoms may diffuse much faster than the other, so that the slow diffusers may serve the role of an elastic network. For example, some materials can absorb and release large amounts of hydrogen, making them candidates for hydrogen 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 solid 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)
- K.J. Zhao, M. Pharr, J. J. Vlassak and Z.G. Suo. Large plastic deformation in high-capacity lithium-ion batteries caused by charge and discharge. Journal of American Ceramic Society. DOI: 10.1111/j.1551-2916.2011.04432.x (http://www.seas.harvard.edu/suo/papers/241.pdf).

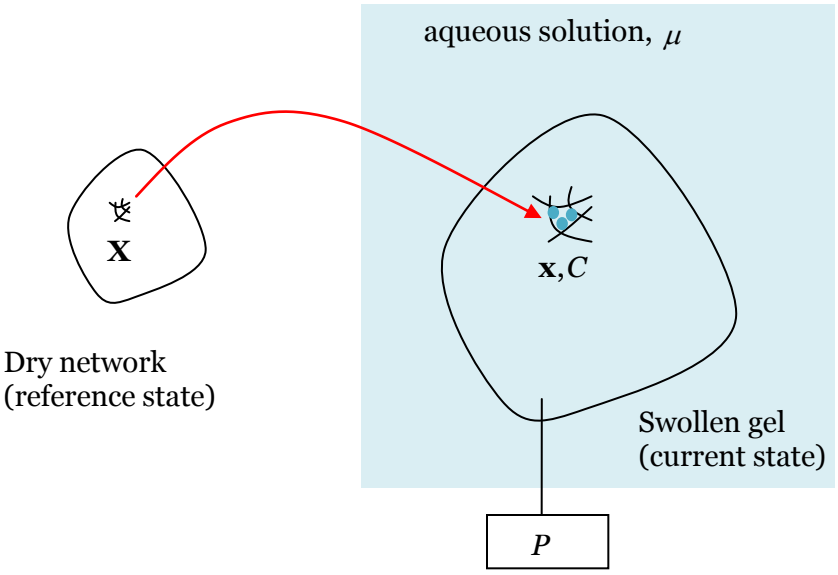
Short-time limit and long-time limit. When a gel is subject to a sudden change in mechanical load, which is then held constant subsequently, the gel evolves over time. Two limiting states of the gel can be analyzed without studying the time-dependent process. In the short-time limit, the solvent molecules inside the gel do not yet have time to redistribute, but the mechanical equilibrium has already been established. Consequently, the concentration field in the gel is known, $C(\mathbf{X})$, and the boundary-value problem is the same as that in the theory of elasticity. The short-time limit corresponds to local rearrangement of molecules.



In the long-time limit, the gel

has reached the equilibrium with both the mechanical load and the external solvent. The chemical potential μ is homogeneous throughout the gel, and is prescribed by the external solvent. The long-time limit corresponds to long range rearrangement of molecules. The long-time limiting state is considered in a separate set of notes, entitled "elastomer in equilibrium with forces and solvent" (http://imechanica.org/node/10179).

Here we will focus on the time-dependent process of the solvent migrating in the network.



Kinematics of the gel. Consider an elastomeric gel. When the gel is in the reference configuration, an element of the network occupies in the space a place with coordinates $\mathbf{X}$, which we will use to name the element. In the reference configuration, let $dV(\mathbf{X})$ be an element of volume, $dA(\mathbf{X})$ be an element of area, and $N_K(\mathbf{X})$ be the unit vector normal to the element of area.

At time t, the gel is in the current configuration, and the element $\mathbf{X}$ moves in the space to a new place with coordinates $\mathbf{x}$. The function

$$\mathbf{x} = \mathbf{x}(\mathbf{X}, t)$$

specifies the deformation of the network.

Let C be the nominal concentration of the solvent in the gel in the current configuration. That is, $CdV(\mathbf{X})$ is the number of solvent molecules in the element of volume. The function

$$C = C(\mathbf{X}, t)$$

specifies the distribution of the solvent in the gel.

The two functions, $\mathbf{x}(\mathbf{X},t)$ and $C(\mathbf{X},t)$, specify the kinematics of the gel. The object of the theory is to evolve the two fields in time.

As usual, the deformation gradient of the network is defined as

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

We will use $\mathbf{F}$ to characterize the state of deformation of an element of the gel.

Conserving the number of solvent molecules. Let $C(\mathbf{X},t)$ be the nominal concentration of the solvent in the gel in the current configuration, namely, $C(\mathbf{X},t)dV(\mathbf{X})$ is the number of solvent molecules in the element of volume. Let $J_K(\mathbf{X},t)$ be the nominal flux of the solvent in the gel, namely, $J_K(\mathbf{X},t)N_K(\mathbf{X})A(\mathbf{X})$ is the number of the solvent molecules per unit time migrating across the element of area. Imagine that the network is attached with a field of pumps, which inject the solvent into the gel. In the current configuration, the pumps inject $r(\mathbf{X},t)dV(\mathbf{X})$ number of the solvent molecules into the element of volume per unit time, and $i(\mathbf{X},t)dA(\mathbf{X})$ number of the solvent molecules into the element of area per unit time. We assume that no chemical reaction occurs, so that the number of the solvent molecules is conserved, namely,

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

in the volume of the gel, and

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

on the part of the surface of the gel where the pumps inject solvent molecules.

Conditions of mechanical equilibrium. Imagine that the network is attached with a field of weights, which apply forces to the gel. In the current configuration, the weights apply a force $B_i(\mathbf{X},t)dV(\mathbf{X})$ to the element of volume, namely, $B_i(\mathbf{X},t)$ is the applied forces in the current configuration per unit volume of the reference configuration. Similarly, the weights apply a force $T_i(\mathbf{X},t)dA(\mathbf{X})$ to the element of area, namely, $T_i(\mathbf{X},t)$ is the applied forces in the current configuration per unit area of the reference configuration. The conditions of local equilibrium require that the inertia effect be negligible and that the viscoelastic process in the element be fully relaxed, so that

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

in the volume of the gel, and

$$s_{iK}(\mathbf{X},t)N_K(\mathbf{X}) = T_i(\mathbf{X},t)$$

on the part of the surface of the gel where forces are applied.

Conditions of local equilibrium. Elements of the gel in different locations may not be in equilibrium with each other, and this disequilibrium motivates the solvent to migrate. Each differential element of the gel, however, is taken to be locally in a state of equilibrium. That is, the migration of the solvent is such a slow process that the effect of inertia is negligible, the viscoelastic process in the element has enough time to relax, and the solvent in the element has enough time to equilibrate with the solvent in the pump attached to the element. Furthermore, the gel is assumed to be held at a constant temperature.

Let $s_{iK}(\mathbf{X},t)$ be the field of stress, and $\mu(\mathbf{X},t)$ be the field of the chemical potential of the solvent. Let W be the free energy in a block in the current state divided by the volume of the block in the reference state. That is, namely, $WdV(\mathbf{X})$ is the free energy associated with the element of the gel. Because the element of the gel is in local equilibrium, the change in the free energy equals the work done by the forces and by the chemical potential:

$$\delta W = s_{iK}\delta F_{iK} + \mu\delta C .$$

The free energy is taken to be a function of the deformation gradient and the concentration, $W(\mathbf{F},C)$. To ensure that the free energy is unchanged when the body undergoes a rigid-body rotation, we requires that W depends on **F** through the Green deformation tensor $F_{iK}F_{iL}$. Associated with any virtual changes, δF_{iK} and δC, the free energy of the material element of volume changes by

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

A comparison of the two expressions for δW gives that

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

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

Conditions of local equilibrium in terms of $\hat{W}(\mathbf{F},\mu)$. Write

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

This equation, together with $\delta W = s_{iK}\delta F_{iK} + \mu\delta C$, gives that

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

Regard $\hat{W}$ as a function of **F** and μ. According to the differential calculus,

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

A comparison of the two expressions for $\delta\hat{W}$ gives that

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

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

Kinetics of migrating solvent. 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,

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

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

$$\int J_K\frac{\partial\mu}{\partial X_K}dV \le 0 .$$

This inequality must hold for any arbitrary fields of the flux J_K. One common way to do this is to adopt a kinetic law

$$J_K(\mathbf{X},t) = -M_{KL}\frac{\partial\mu(\mathbf{X},t)}{\partial X_L},$$

where M_{KL} is a positive-definite tensor, known as the mobility tensor.

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

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

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

on an interface.

Balance of forces:

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

in the volume of the body, and

$$s_{iK}N_K=T_i$$

on an interface.

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

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

Boundary and initial conditions. 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 $i(\mathbf{X},t)$ 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 $M_{KL}(\mathbf{F},\mu)$.

Adding volumes (molecular incompressibility). As discussed in the notes on elastomers in equilibrium with forces and solvents (http://imechanica.org/node/10179), a commonly adopted approximation is that the volume of the gel is the sum of the volume of the dry network and the volume of the solvent:

$$1+\upsilon C=\det(\mathbf{F}).$$

One may choose to invoke this approximation.

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. An example is described by Hong, Zhao, Zhou and Suo, J. Mech. Phys. Solids 56, 1779-1793 (2008).
- Develop finite element method to analyze transient processes in gels undergoing large deformation. See Zhang, Zhao, Suo, Jiang, J. Appl. Phys., 105, 093522 (2009). Chester and Anand, J. Mech. Phys. Solids 58, 1879 (2010).
- Apply the theory to important phenomena. For example, instability is commonly observed during the swelling of a gel.