

## Poroelasticity, or diffusion in elastic solids

**Migration of matter in an elastic solid.** A sponge is an elastic solid with connected pores. When immersed in water, the sponge absorbs water. When a saturated sponge is squeezed, water will come out. More generally, the subject is known as diffusion in elastic solids, or elasticity of fluid-infiltrated porous solids, or poroelasticity. The theory has been applied to diverse phenomena. Here are a few examples.

*Consolidation of soils.* A soil is a composite of solid particles and fluids (mainly water). Particles in the soil 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 will flow out gradually, so that the soil will deform over some time. This process is known as consolidation.

- M.A. Biot, General theory of three-dimensional consolidation, *Journal of Applied Physics* 12, 155-164 (1941).
- J. Bear, *Dynamics of fluids in porous media*. Dover reprint, 1988.
- 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](http://esag.harvard.edu/rice/e2_Poroelasticity.pdf)).
- J.R. Rice and M.P. Cleary, Some basic stress-diffusion solutions for fluid-saturated elastic porous media with compressible constituents. *Reviews of Geophysics and Space Physics* 14, 227-241 (1976).
- H. F. Wang, *Theory of linear poroelasticity with applications to geomechanics and hydrogeology*. Princeton University Press, 2000.

*Swelling of gels.* A gel is a composite of a network of crosslinked molecules, and a solvent consisting of all other molecules that permeate in the interstices of the network, but are not linked to the network. The network is elastic, while the solvent can migrate through the interstices of the network. The elasticity of the network and migration of the solvent are coupled: the network swells where the solvent accumulates, and the solvent migrates in response to the deformation of the network. The gel is called a hydrogel when the solvent is water, or an [aerogel](#) when the solvent is a gas.

- J. Dolbow, E. Fried, H. Ji, Chemically induced swelling of hydrogels. *Journal of the Mechanics and Physics of Solids* 52, 51-84 (2004).
- A. Sidorenko, T. Krupenkin, A. Taylor, P. Fratzl, and J. Aizenberg, Reversible switching of hydrogel-actuated nanostructures into complex micropatterns. *Science* 315, 487-490 (2007).

*Fluid migration in tissues.* Nearly all living tissues are porous and elastic, with fluid migrating in the pores inside the tissues to transport nutrients and wastes.

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

*Diffusion in crystals.* Metals and ceramics are often in the form of alloys, consisting of dissimilar atoms. Some atoms diffuse much faster than other atoms, 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 alloys, 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>)

This lecture will focus on diffusion in elastic solids. Historically, the theory coupling diffusion and elasticity has caused a great deal of confusion. It might be helpful if we start with elementary ideas.

**Thermodynamics of a fluid of single species of molecules.** We have studied chemical potential in a previous lecture (<http://imechanica.org/node/911>). The chemical potential of a species of molecules in a system is defined as the increase of the free energy of the system upon gaining one molecule of the species.

A thermodynamic state of a fluid (either a gas or a liquid) of a single species of molecules is characterized by three degrees of freedom. For example, we can use the Gibbs function  $G(p, T, N)$  to characterize all possible thermodynamic states of the fluid. A particular thermodynamic state of the fluid has a homogeneous field of pressure  $p$  and temperature  $T$ . The Gibbs function is proportional to the number of molecules,  $N$ . Thus,

$$G(p, T, N) = N\mu(p, T),$$

where the free energy per molecule,  $\mu$ , is the chemical potential. Because the dependence of the Gibbs function on  $N$  is trivial, this family of thermodynamic states are essentially characterized by,  $\mu(p, T)$ , a function of two variables.

Associated with small changes in the pressure and the temperature, the chemical potential changes by

$$\delta\mu = \bar{V}\delta p - \bar{S}\delta T,$$

where  $\bar{V}$  is the volume of the fluid divided by the number of molecules, and  $\bar{S}$  is the entropy of the fluid divided by the number of molecules. In practice, the functions  $\bar{V}(p, T)$  and  $\bar{S}(p, T)$  are determined by experiments.

**Chemical potential of an incompressible liquid.** We now hold the temperature constant, but vary the pressure, so that the chemical potential varies by

$$\delta\mu = \bar{V}\delta p.$$

For an incompressible liquid, the volume per molecule,  $\bar{V}$ , is independent of the pressure. Integrating with respect to the pressure, we obtain that

$$\mu(p, T) = \mu(p_0, T) + \bar{V}(T)(p - p_0).$$

This result is often written as

$$\mu = \bar{V}p,$$

with the understanding that  $\mu$  is the chemical potential at pressure  $p$  relative to the chemical potential at zero pressure, while the temperature is fixed.

**Chemical potential of an ideal gas.** Recall the ideal gas law,  $pV = NT$ , so that  $\bar{V} = T/p$ . Integrating  $\delta\mu = \bar{V}\delta p$ , we obtain that

$$\mu(p, T) = \mu(p_0, T) + T \log(p/p_0).$$

This relation holds for ideal gas.

**Equilibrating a liquid and a vapor of the same species of molecules.**  
Consider a liquid in contact with a vapor of the same species of molecules. The composite of the gas and the liquid is a system has a fixed pressure  $p$ , a fixed temperature  $T$ , and a fixed total number of molecules  $N_{tot}$ . Molecules can escape from the liquid and enter the vapor (evaporation), or the other way around (condensation). Consequently, the number of molecules in the vapor,  $N$ , is an internal variable of the composite system.

weight
gas
liquid

Let  $\mu_l(p, T)$  be the Gibbs function per molecule in the liquid, and  $\mu_g(p, T)$  be the Gibbs function per molecule in the gas. When the gas has  $N$  molecules, the liquid will have  $N_{tot} - N$  molecules. The Gibbs function for the composite system is the sum of the free energy of the gas and that of the liquid:

$$G(p, T, N) = N\mu_g(p, T) + (N_{tot} - N)\mu_l(p, T).$$

When the vapor equilibrates with the liquid, the Gibbs function of the composite minimizes, so that  $\partial G(p, T, N) / \partial N = 0$ , namely,

$$\mu_g(p, T) = \mu_l(p, T).$$

Thus, when two systems are in contact, allowing a species of molecules to go between the two systems, the two systems in equilibrium will have the same chemical potential of the species.

(Incidentally, the above conclusion is general. When a species of molecules is allowed to relocate throughout a system, in equilibrium the chemical potential of this species is uniform everywhere in the system. The situation is analogous to the temperature, when energy is allowed to relocate.)

Now, let us return to the vapor and the liquid. The equilibrium condition  $\mu_g(p, T) = \mu_l(p, T)$  requires that the pressure be a function of the temperature. This functional dependence can be made explicit as follows. The equilibrium condition  $\mu_g(p, T) = \mu_l(p, T)$  holds for any pressure and temperature. For small changes in the pressure and temperature, we can differentiate the equation on both sides, so that

$$\bar{V}_g \delta p - \bar{S}_g \delta T = \bar{V}_l \delta p - \bar{S}_l \delta T.$$

We regard the pressure as a function of the temperature,  $p(T)$ , so that

$$\frac{\delta p}{\delta T} = \frac{\bar{S}_g - \bar{S}_l}{\bar{V}_g - \bar{V}_l}.$$

This result is known as the Clapeyron equation.

The above result is exact. We next make a few useful approximations. Note that  $\bar{V}_g \gg \bar{V}_l$ , so that we will neglect  $\bar{V}_l$  in the denominator. Furthermore, we will approximate the vapor as an ideal gas, so that  $\bar{V}_g = T/p$ . By definition, the entropy difference is

$$\bar{S}_g - \bar{S}_l = \frac{H_{vap}}{T},$$

where  $H_{vap}$  is the enthalpy of vaporization, which is essentially the energy of the molecular bonds in the liquid. Inserting these approximations into the Clapeyron equation, we obtain that

$$\frac{\delta p}{\delta T} = \frac{H_{vap}}{T^2}$$

If we neglect the weak temperature dependence of  $H_{vap}$ , we obtain that

$$\log(p/p_0) = -H_{vap} \left( \frac{1}{T} - \frac{1}{T_0} \right).$$

This expression is known as the Clausius-Clapeyron equation.

The vapor pressure as a function of the temperature can be determined experimentally. For example, here are the experimental data for water vapor.

Pressures of water vapor in equilibrium with liquid water at several temperatures

T (C)	T ( $10^{-2}$ eV)	1/T (1/eV)	p (kPa)
0	2.36	42.4	0.61
10	2.45	40.8	1.23
20	2.52	39.7	2.34
30	2.61	38.3	4.24
40	2.70	37.0	7.38
50	2.79	35.8	12.33
100	3.22	31.1	101.33
37	2.68	37.3	6.28

Recall the conversion between different units of temperature:

$$T(\text{eV}) = (T(\text{C}) + 273.25) \frac{1.38 \times 10^{-23} \text{ J/K}}{1.60 \times 10^{-19} \text{ eV/J}}.$$

The vapor pressure increases with the temperature. At the freezing point, the vapor pressure is 0.61 Pa. At 100C, the vapor pressure is 101.33 kPa. One can plot  $\log p$  against  $1/T$ . On this plot, all the data points are approximately on a straight line. The slope of this line is the enthalpy of vaporization. These data give  $H_{vap} \approx 0.45\text{eV}$ .

**Humidity.** The absolute humidity may be measured by the number of water molecules per unit volume,  $N/V$ . If we model the vapor as an ideal gas,  $N/V = p/T$ .

At a given temperature, when the air is in equilibrium with the liquid water, we say that the air is saturated with water. Thus, at the body temperature 37C, the saturated vapor has the absolute humidity of  $1.46 \times 10^{24}$  molecules/m<sup>3</sup>.

If a given volume of air contains fewer water molecules, the number of molecules in the air divided by that in the saturated vapor is called the relative humidity (RH). If the vapor is modeled as an ideal gas, the relative humidity is also the pressure of water in the given vapor divided by that in the saturated vapor. We write the chemical potential of water in the air as

$$\mu = T \log RH,$$

with the understanding that the chemical potential is relative to that of the water molecules in a saturated water at the same temperature.

The lung is always saturated with water vapor at the body temperature (37C), but the atmospheric air may not be. In winter, the cold air outside has low water content even at 100% relative humidity. When the cold air enters a warm room, the relative humidity in the room will

reduce below 100% at the room temperature. We will feel uncomfortable. Also, water inside the warm room will condense on cold window panes.

**Equilibrate a gel with a weight and a moist environment.** We have outlined the thermodynamics of hydrogels in a previous lecture (<http://imechanica.org/node/911>). A gel is subject to a force  $P$ , which may be varied by hanging different weights to the gel. The gel is also in a moist environment, with the chemical potential of water in the environment being  $\mu$ , which can be varied by changing the partial pressure of the water in the environment. We may regard both  $P$  and  $\mu$  as external loads applied to the gel. Let  $l$  be the displacement of the weight, and  $N$  be the number of water molecules absorbed by the gel. When the gel is in equilibrium with the weight and the moisture, what are the displacement and the water content in the gel?

When dropping by a small displacement,  $\delta l$ , the weight does work  $P\delta l$  or, equivalently, the weight reduces its free energy by  $P\delta l$ . If the weight is fixed, the free energy of the weight is  $-Pl$ .

Upon giving a number of water molecules,  $\delta N$ , to the gel, the moisture does work  $\mu\delta N$ , or equivalently, the moisture reduces its free energy by  $\mu\delta N$ . If the moisture is a large reservoir of water molecules, so that the chemical potential  $\mu$  is fixed as the gel absorbs water. The moisture of a fixed chemical potential has the free energy  $-\mu N$ .

At the fixed temperature, the gel is characterized by the Helmholtz function  $F(l, N)$ . Associated with the small changes  $\delta l$  and  $\delta N$ , the free energy of the gel increases by

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

The composite of the gel, the weight and the moisture is a system in thermal contact with a reservoir of energy, which holds the system at a fixed temperature. We only permit energy to go between the composite and the reservoir; we block all other modes of interaction between the composite and the reservoir. The displacement  $l$  and the number of water molecules  $N$  in the gel are the internal variables of the composite. The total free energy of the composite system,  $\Pi$ , is the sum of the free energy of the gel, the weight and the moisture, and is a function of  $l$  and  $N$ , namely,

$$\Pi(l, N) = F(l, N) - Pl - \mu N.$$

In equilibrium, the free energy of the composite minimizes, so that the variation of the total free energy vanishes:

$$\delta F - P\delta l - \mu\delta N = 0.$$

Consequently, to equilibrate with the gel, the weight and the chemical potential of water molecules in the moisture must be

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

The gel couples chemistry and mechanics: a change in the chemical potential of water molecules in the moisture will cause a change in the displacement of the weight, and a change in the weight will cause water molecules to diffuse into or out of the gel.

The above theory is applicable when the gel is inhomogeneous and of any size. For example, the theory is applicable even when the gel is a single molecule. We next extend the theory into a field theory. When the weight and the chemical potential of the moisture 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, and the size is larger than

the size of microstructure, 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, as well as the time needed for a body to settle to a new configuration after a load is applied.

**A homogeneous field of stress and water concentration.** To formulate a field theory, we will need intensive variables. First consider a rod in a homogenous state. Any state may be used as a reference state. In the reference state, the rod has a cross-sectional area  $A$ , length  $L$ , and volume  $V = AL$ . In the current state, subject to a weight  $P$  and a moisture of chemical potential  $\mu$ , the rod has the length  $l$ , and the number of water molecules  $N$ .

Define the stretch by

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

Define the nominal stress by

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

The work done by the weight is

$$P\delta l = Vs\delta\lambda.$$

Define the nominal concentration by

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

The work done by the chemical potential of the moisture is

$$\mu\delta N = V\mu\delta C.$$

The Helmholtz function of the rod is  $F(l, N)$ . Define the nominal density of the Helmholtz free energy by

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

This density is a function  $W(\lambda, C)$ . Its differential 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 moisture, the free energy of the composite of the rod, the weight and the moisture minimizes, so that for any small changes in the displacement and the number of molecules, the variation of the total free energy of the composite vanishes:

$$\delta F - P\delta l - \mu\delta N = 0.$$

Divide this equation by the volume of the rod in the reference state,  $V$ , and we obtain that

$$\delta W - s\delta\lambda - \mu\delta C = 0.$$

When the rod equilibrates with the weight and the chemical potential, we obtain that

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

**Alternative free-energy functions.** We may define an alternative free energy as

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

Thus, associated with small changes, this new free energy changes by

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

The free energy is a function of the stretch and chemical potential. The stress and the concentrations are given by

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

Another useful alternative free-energy function is

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

Thus, associated with small changes, this new free energy changes by

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

The free energy is a function of the stretch and chemical potential. The stress and the concentrations are given by

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

**Inhomogeneous, equilibrium field.** We now expose an elastic network to a moist environment held at a fixed chemical potential  $\mu$ , allowing water molecules to enter the network. We also hang weights on the network. After some time, the body becomes an elastic network saturated with water, in equilibrium with the moist environment and the weights. In equilibrium, the chemical potential will be homogenous in the body, and takes the value of the moist environment. The field deformation of the network, however, can be inhomogeneous. We next set out to formulate a theory to determine the deformation.

We take any particular state of the network as the 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  $\mathbf{x}(\mathbf{X}, t)$  describes the deformation of the network. We will retain the time dependence explicitly, which we will need later in formulating the theory for a gel not in equilibrium.

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

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

Consider a block of the network around  $\mathbf{X}$ , of volume  $dV(\mathbf{X})$ . The network may contain interfaces between dissimilar parts. Let  $N_K(\mathbf{X})dA(\mathbf{X})$  be an area element of an interface, where  $dA(\mathbf{X})$  is the area of the element, and  $N_K(\mathbf{X})$  is 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 virtual deformation of the network,  $\delta \mathbf{x}(\mathbf{X})$ , the weights do work

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

The free energy of the weights reduces by this amount.

The concentration of the molecules,  $C(\mathbf{X}, t)$ , is the number of the molecules inside the block divided by the volume of the block. Associated with a virtual change in the concentration,  $\delta C(\mathbf{X})$ , the number of molecules enter the body is  $\int \delta C dV$ , so that the moist environment does work

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

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,  $\delta F_{iK}$  and  $\delta C$ , the free energy of the material element of volume changes by

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

The body, the weights and the moist environment constitute a composite system. The total free energy of the composite system,  $\Pi$ , is the sum of the free energy of the constituents. The variation of the total free energy is

$$\delta \Pi = \int \delta W dV - \int B_i \delta x_i dV - \int T_i \delta x_i dV - \mu \int \delta C dV .$$

When the weights and the chemical potential are held constant, the field of deformation and concentration become internal variables, and  $\Pi$  is a functional of the fields  $\mathbf{x}(\mathbf{X})$  and  $C(\mathbf{X})$ .

Inserting the expression for  $\delta W$  into the above, and applying the divergence theorem, we obtain that

$$\begin{aligned} \int \frac{\partial W}{\partial F_{iK}} \frac{\partial \delta x_i}{\partial X_K} dV &= \int \left[ \frac{\partial}{\partial X_K} \left( \frac{\partial W}{\partial F_{iK}} \frac{\partial \delta x_i}{\partial X_K} \right) - \frac{\partial}{\partial X_K} \left( \frac{\partial W}{\partial F_{iK}} \right) \delta x_i \right] dV \\ &= \int \left[ \left( \frac{\partial W}{\partial F_{iK}} \right)^- - \left( \frac{\partial W}{\partial F_{iK}} \right)^+ \right] N_K \delta x_i dA - \int \frac{\partial}{\partial X_K} \left( \frac{\partial W}{\partial F_{iK}} \right) \delta x_i dV \end{aligned}$$

The surface integral extends over the area of all interfaces. Consequently, the variation of the total free energy is

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

In equilibrium, the total free energy vanishes for arbitrary virtual deformation and virtual changes in 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

$$\left[ \left( \frac{\partial W}{\partial F_{iK}} \right)^- - \left( \frac{\partial W}{\partial F_{iK}} \right)^+ \right] N_K = T_i ,$$

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

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



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

Because the chemical potential in the environment is prescribed, and the same value is reached inside the body, it will be convenient to regard  $\mu$  as an independent variable. Take the Lagrange transformation:

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

so that

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

and

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

**Invariance under rigid-body rotation.** When the entire system in the current state undergoes a rigid-body rotation, the nominal electric displacement  $\tilde{\mathbf{D}}$  is invariant, but the deformation gradient,  $F_{iK}$ , varies. To ensure that  $W$  is invariant under rigid-body rotation, we invoke the Lagrangian 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  $W(\mathbf{L}, \tilde{\mathbf{D}})$ . The nominal stress and the nominal electric field are obtained from partial derivatives:

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

**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  $C$ :

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

**Diffusion in a rigid network.** We now review diffusion of a molecular species 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  $N_K(\mathbf{X})dA(\mathbf{X})$  be an area element of an interface, where  $dA(\mathbf{X})$  is the area of the element, and  $N_K(\mathbf{X})$  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 body. On a geological scale, for example, such a pump can be a well. Let the number of the molecules injected into a volume element be  $r(\mathbf{X}, t)dV(\mathbf{X})$ , and into an interface element be  $j(\mathbf{X}, t)dA(\mathbf{X})$ . The molecules also diffuse in the network. Let  $J_K(\mathbf{X}, t)$  be the flux of the molecules, namely, the number molecules per unit time crossing per unit area in direction  $X_K$ . We assume that no chemical reaction occurs, so that the number of the molecules is conserved, namely,

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

in the volume, and

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

on an interface.

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

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

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:

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

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, 2<sup>nd</sup> edition. Cambridge University Press, 1997.
- J. Crank, The mathematics of diffusion, 2<sup>nd</sup> 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:

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

where  $p(\mathbf{X},t)$  is the pressure in the fluid,  $\eta$  the viscosity of the fluid,  $\bar{V}$  is the volume per molecule, and  $k$  has the dimension of length squared.  $k$  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

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

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 nonequilibrium processes.** The above theories seem somewhat *ad hoc*. A more potent recipe to concoct such theories is the thermodynamics of nonequilibrium process.

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. The power delivered by the pumps is

$$\int \mu r dV + \int \mu j dA.$$

This is also the rate at which the free energy of the pumps decreases.

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

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

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

The composite of the body and the pumps is a system in thermal contact with a reservoir. The free energy of the composite system changes at the rate

$$\frac{\delta \Pi}{\delta t} = \int \frac{\delta W}{\delta t} dV - \int \mu r dV - \int \mu j dA.$$

Due to diffusion, the composite system is out of equilibrium. According to thermodynamics, the free energy of the composite system cannot increase, namely,

$$\frac{\delta \Pi}{\delta t} \leq 0,$$

or

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

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

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

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 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

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

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

$$J_K(\mathbf{X}, t) = -\frac{TM}{C} \frac{\partial C(\mathbf{X}, t)}{\partial X_K}.$$

A comparison with Fick's law gives that

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

This is Einstein's relation.

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

$$\mu = \bar{V} p.$$

Inserting this expression into the kinetic law, we obtain that

$$J_K(\mathbf{X}, t) = -M\bar{V} \frac{\partial p(\mathbf{X}, t)}{\partial X_K}.$$

A comparison with Darcy's law gives that

$$M = \frac{k}{\eta \bar{V}^2}.$$

- 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,  $\delta F_{iK}$  and  $\delta C$ , the free energy of the material element of volume changes by

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

Associated with a virtual rate of molecular injection,  $r$  and  $j$ , as well as the virtual velocity  $\delta x_i / \delta t$ , the total free energy of the composite system of the body, the weights and the pumps changes at the rate

$$\frac{\delta \Pi}{\delta t} = \int \frac{\delta W}{\delta t} dV - \int B_i \frac{\delta x_i}{\delta t} dV - \int T_i \frac{\delta x_i}{\delta t} dA - \int \mu r dV - \int \mu j dA.$$

Inserting the expression for  $\delta W$  into the above, and apply the divergence theorem, we obtain that

$$\begin{aligned} \frac{\delta \Pi}{\delta t} = & \int \left[ \left( \left( \frac{\partial W}{\partial F_{iK}} \right)^- - \left( \frac{\partial W}{\partial F_{iK}} \right)^+ \right) N_K - T_i \right] \frac{\delta x_i}{\delta t} dA - \int \left[ \frac{\partial}{\partial X_K} \left( \frac{\partial W}{\partial F_{iK}} \right) + B_i \right] \frac{\delta x_i}{\delta t} dV \\ & + \int \left( \frac{\partial W}{\partial C} - \mu \right) j dA + \int \left( \frac{\partial W}{\partial C} - \mu \right) r dV \\ & + \int J_K \frac{\partial}{\partial X_K} \left( \frac{\partial W}{\partial C} \right) dV \end{aligned}$$

Thermodynamics dictate that the free energy of the composite system should never increase, namely,

$$\frac{\delta \Pi}{\delta t} \leq 0.$$

This inequality must hold for any arbitrary  $r$ ,  $j$  and  $J_K$ ,  $\delta x_i / \delta t$ . We will assume local equilibrium, so that the first 4 terms vanish:

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

in volume,

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

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.

*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

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

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

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

on an interface.

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

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

**Linear poroelasticity.** If disturbance from the reference state is small, we may approximate material laws 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  $\hat{W}(\sigma, \mu)$  is a quadratic form:

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

Where  $E$ ,  $\alpha$  and  $\beta$  are material constants. Thus, the material laws are

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

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

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.

The coefficient  $\alpha$  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  $\alpha$  will have the same unit as that of coefficient of thermal expansion.

Generalizing to a tensor form is straightforward:

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

For an isotropic material, we need a total 4 material constants: 2 for the compliance tensor, 1 for the interaction tensor  $\alpha_{ik}$ , and 1 constant  $\beta$ . The material laws are written as

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

There are many ways to regroup these four material constants.

We can also use the strains as independent variables:

$$\sigma_{kk} = \frac{E}{1-2\nu} (e_{kk} - 3\alpha\mu)$$

so that

$$\begin{aligned}\sigma_{ij} &= \frac{E}{1+\nu} \left( e_{ij} + \frac{\nu}{1-2\nu} e_{kk} \delta_{ij} \right) - \frac{E}{1-2\nu} \alpha \mu \delta_{ij} \\ C &= \frac{E\alpha}{1-2\nu} e_{kk} + \left( \beta - \frac{3E\alpha^2}{1-2\nu} \right) \mu\end{aligned}$$

When deformation is small, we may disregard the difference between the reference and the current state in writing equilibrium equations. Let  $\sigma_{ij}$  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

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

**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

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

This result is analogous to the stress due to misfit in the coefficient of thermal expansion. The concentration of water changes by

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

**Stress 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, by the surface layer will change moisture content. Let the change in the chemical potential in the moisture be  $\mu_0$ . The chemical potential of water in the body is  $\mu(z, t)$ . 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

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

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

$$C = 2\alpha\sigma + \beta\mu = \beta' \mu, \quad \beta' = -\frac{2E\alpha^2}{1-\nu} + \beta.$$

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

$$\frac{\partial \mu}{\partial t} = \frac{M}{\beta'} \frac{\partial^2 \mu}{\partial z^2}.$$

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

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



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

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

The distribution of stress is similar.

**Analysis of a soil test (Biot, 1941).** A column of soil, height  $h$ , is saturated with water. At time zero, a stress  $\sigma_z = \sigma_0$  is applied to the top surface of the soil. The column is confined laterally in a rigid sheath so that no lateral expansion can occur. 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.

*Equilibrium state.* After some time, the column will attain equilibrium with the load. The chemical potential of water in the soil will become the same as 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:

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

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 equilibrate with the compression, the total number of water molecules escaped from the soil is  $C$  times the volume of the column.

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

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

Here we can solve for the entire time history. In this example, the stress state is homogenous at all time:

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

The chemical potential, concentration and strain evolve with time. The concentration is

$$C = \alpha \sigma_{kk} + \beta \mu = \frac{1+\nu}{1-\nu} \alpha \sigma_0 + \beta \mu$$

Substitute into

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

And we obtain that

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

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:

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

The amount of water escaped may be calculated from

$$\frac{\int_0^h C(z,t) dz}{hC_{eq}} = 1 + \frac{32}{\pi^3} \sum_{n=1}^{\infty} \frac{(-1)^n}{(2n-1)^3} \exp\left[-\left(\frac{2n-1}{2} \pi\right)^2 \frac{t}{\tau}\right].$$

**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  $\mu_0$ . The migration of molecules along the crack is taken to be so fast that the chemical potential in the crack also drops by  $\mu_0$ . 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  $\kappa$  is a dimensionless function of Poisson's ratio  $\nu$  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  $\sigma_0$  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  $\nu$  and the interaction parameter

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