Polyelectrolyte gels

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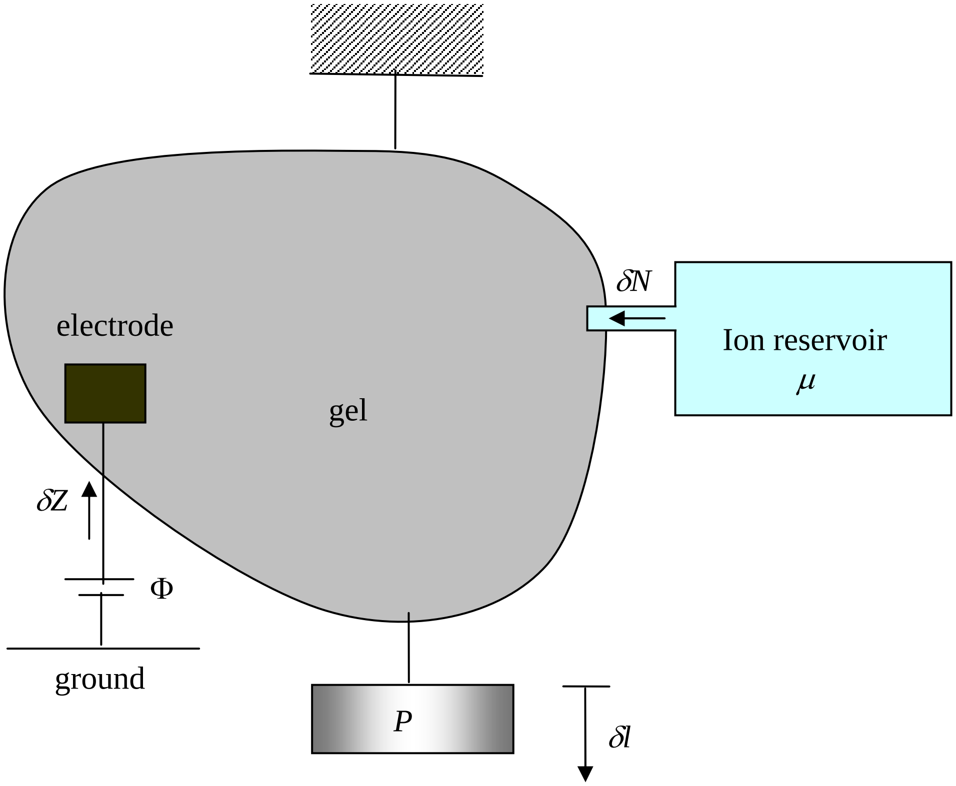
These notes attempt to address the concerns raised by Weil Hong (http://imechanica.org/node/1641#comment-3457), and supplement the notes on Poroelasticity, diffusion in an elastic solid (http://imechanica.org/node/987). The main purpose is to add electrical effects, so that the theory will apply to polyelectrolyte gels. I'll adopt an approach developed by Suo, Zhao and Greene for elastic dielectric (JMPS http://dx.doi.org/10.1016/j.jmps.2007.05.021, preprint: http://imechanica.org/node/635). The theory, however, has been developed by many people in many ways. See references at the end of the notes.



Work done on a gel. Consider three ways of doing work. A weight applies a force P, drops by distance δl, and does work $P\delta l$. A battery maintains a voltage Φ between the electrode and the ground, pumps electric charge δZ from the ground to an electrode, and does work $\Phi\delta Z$. We may as well identify the charge carriers through the battery to be electrons. We assume that electrons cannot migrate in the gel. A reservoir maintains the electrochemical potential μ of a species of ions, injects δN number of the ions into the gel, and does work $\mu\delta N$. We assume that the ions can migrate in the gel.

If several species of ions are present, we may imagine one reservoir for every species. Each reservoir maintains the electrochemical potential of one species of ions, and is connected to the gel through a semi-permeable link, so that the reservoir can only inject this species of ion into the gel. An electrically neutral species of molecules can also have its own reservoir and link. In the model, a species of neutral molecules is treated the same as a species of ions, except that the valance of the neutral species is set to be zero.

This description is applicable to a single macromolecule, a cell, or a large system. We next develop a field theory of a gel.

Deformation of an elastic network. A gel consists of an elastic network and a solvent. Both the network and the solvent are possibly ionic. Imagine a field of markers are attached to the network. We take the network at a particular time as a reference state. and name each marker using its coordinates $\mathbf{X}$ in the reference state. In the reference state, let $dV(\mathbf{X})$ be an element of volume in the reference state, and let $N_K(\mathbf{X})dA(\mathbf{X})$ be an 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 interface between media labeled as – and +, pointing toward medium +.

At time t, the marker $\mathbf{X}$ moves to a place with coordinate $\mathbf{x}$. The function $\mathbf{x}(\mathbf{X},t)$ describes the deformation of the network. The deformation gradient is

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

Nominal stress. Imagine that we hang a field of weights on the elastic network. In the current state at time t, let the force due to the weights on a material element of volume be $\mathbf{B}(\mathbf{X},t)dV(\mathbf{X})$, and on a material element of an interface be $\mathbf{T}(\mathbf{X},t)dA(\mathbf{X})$.

Define the nominal stress $s_{iK}(\mathbf{X},t)$ such that the following equation

$$\int s_{iK}\frac{\partial \Delta_i}{\partial X_K}dV = \int B_i\Delta_i dV + \int T_i\Delta_i dA,$$

holds true for any test function $\Delta_i(\mathbf{X})$.

Applying the divergence theorem, we obtain that

$$\int s_{iK}\frac{\partial \Delta_i}{\partial X_K}dV = \int\left[\frac{\partial(s_{iK}\Delta_i)}{\partial X_K} - \frac{\partial s_{iK}}{\partial X_K}\Delta_i\right]dV = \int\left(s_{iK}^- - s_{iK}^+\right)N_K\Delta_i dA - \int\frac{\partial s_{iK}}{\partial X_K}\Delta_i dV.$$

The surface integral extends over the area of all interfaces. Across the interface, $\Delta_i(\mathbf{X})$ is assumed to be continuous, but the stress need not be continuous. Insisting that the defining equation for the nominal stress holds true for any $\Delta_i(\mathbf{X})$, we find that the nominal stress obeys that

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

in the volume of the body, and

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

on the surface of the body.

Nominal electric field. Imagine we attach a field of batteries on the elastic network. Each battery maintains the electric potential of a piece of the network with respect to the ground. We define the nominal electric field as the gradient of the electric potential:

$$\tilde{E}_K(\mathbf{X},t) = -\frac{\partial\Phi(\mathbf{X},t)}{\partial X_K}.$$

The negative sign conforms to the convention that the electric field points from a place of high electric potential to a place of low electric potential.

Nominal electric displacement. In the current state at time t, let the charge on a material element of volume be $Q(\mathbf{X},t)dV(\mathbf{X})$, and the charge on a material element of an interface be $\Omega(\mathbf{X},t)dA(\mathbf{X})$. At time t, the imaginary battery attached to material particle $\mathbf{X}$ has electric potential $\Phi(\mathbf{X},t)$.

Define the nominal electric displacement $\tilde{D}_K(\mathbf{X},t)$ such that

$$\int\left(-\frac{\partial\zeta}{\partial X_K}\right)\tilde{D}_K dV = \int \zeta Q dV + \int \zeta \Omega dA$$

holds true for any test function $\zeta(\mathbf{X})$.

We apply the divergence theorem to the left-hand side, and obtain that

$$\int \frac{\partial\zeta}{\partial X_K}\tilde{D}_K dV = \int\left[\frac{\partial\left(\zeta\tilde{D}_K\right)}{\partial X_K} - \zeta\frac{\partial\tilde{D}_K}{\partial X_K}\right]dV = \int \zeta\left(\tilde{D}_K^- - \tilde{D}_K^+\right)N_K dA - \int \zeta \frac{\partial\tilde{D}_K}{\partial X_K} dV .$$

The test function $\zeta(\mathbf{X})$ is assumed to be continuous across the interface, but the electric displacement need not be continuous across the interface. Insisting that the defining equation for the nominal electric displacement holds true for any $\zeta(\mathbf{X})$, we find that the nominal electric displacement obeys that

$$\frac{\partial\tilde{D}_K(\mathbf{X},t)}{\partial X_K} = Q(\mathbf{X},t)$$

in the volume of the body, and

$$\left(\tilde{D}_K^+(\mathbf{X},t) - \tilde{D}_K^-(\mathbf{X},t)\right)N_K(\mathbf{X},t) = \Omega(\mathbf{X},t).$$

on the surface of the body. These equations express Gauss's law in every current state in terms of the nominal fields.

The number of ions is conserved. Imagine a field of pumps attached to the network, injecting a species of ions into the body. Let the number of the ions 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 ions 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 ions 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

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

on an interface.

The total electric charge including those pumped by the batteries and by the reservoirs:

$$\frac{\delta Q}{\delta t} = \frac{\delta q}{\delta t} + ze\frac{\delta C}{\delta t},$$

$$\frac{\delta\Omega}{\delta t} = \frac{\delta\omega}{\delta t} + zej,$$

where e is the elementary charge and z is the valence of the ion. If several species of ions coexist, we can write similar equations for each species. If a neutral solvent is present, we can write similar equations by setting $z = 0$.

Thermodynamics of nonequilibrium processes. 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, $W\left(\mathbf{F},\tilde{\mathbf{D}},C\right)$. Associated with any virtual changes, the free energy of the material element of volume changes by

$$\delta W = \frac{\partial W\left(\mathbf{F}, \tilde{\mathbf{D}}, C\right)}{\partial F_{iK}} \delta F_{iK} + \frac{\partial W\left(\mathbf{F}, \tilde{\mathbf{D}}, C\right)}{\partial \tilde{D}_K} \delta \tilde{D}_K + \frac{\partial W\left(\mathbf{F}, \tilde{\mathbf{D}}, C\right)}{\partial C} \delta C .$$

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

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

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

$$\begin{aligned} \frac{\delta \Pi}{\delta t} = & \int \left(\frac{\partial W}{\partial F_{iK}} - s_{iK} \right) \frac{\delta F_{iK}}{\delta t} dV + \int \left(\frac{\partial W}{\partial \tilde{D}_K} - \tilde{E}_K \right) \frac{\delta \tilde{D}_K}{\delta t} dV \\ & + \int \left(\frac{\partial W}{\partial C} + ez\Phi - \mu \right) j dA + \int \left(\frac{\partial W}{\partial C} + ez\Phi - \mu \right) r dV \\ & + \int J_K \frac{\partial}{\partial X_K} \left(\frac{\partial W}{\partial C} + ez\Phi \right) dV \end{aligned}$$

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

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

This inequality must hold for any arbitrary *r*, *j*, $\tilde{D}_K$, J_K, $\delta x_i / \delta t$. We will assume local equilibrium, so that the first 4 terms vanish, leading to

$$s_{iK} = \frac{\partial W\left(\mathbf{F}, \tilde{\mathbf{D}}, C\right)}{\partial F_{iK}}, \quad \tilde{E}_K = \frac{\partial W\left(\mathbf{F}, \tilde{\mathbf{D}}, C\right)}{\partial \tilde{D}_K}, \quad \mu = ez\Phi + \frac{\partial W\left(\mathbf{F}, \tilde{\mathbf{D}}, C\right)}{\partial C} .$$

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 momentum:

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

in the volume of the body, and

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

on an interface.

Nominal electric field: $$\tilde{E}_K(\mathbf{X},t) = -\frac{\partial \Phi(\mathbf{X},t)}{\partial X_K}.$$

Gauss's law: $$\frac{\partial \tilde{D}_K(\mathbf{X},t)}{\partial X_K} = Q(\mathbf{X},t)$$

in the volume of the body, and

$$\left(\tilde{D}_K^+(\mathbf{X},t) - \tilde{D}_K^-(\mathbf{X},t)\right)N_K(\mathbf{X},t) = \Omega(\mathbf{X},t).$$

on the surface of the body.

Conservation of ions:

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

in the volume of the network, and

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

on an interface.

The net electric charge:

$$\frac{\delta Q}{\delta t} = \frac{\delta q}{\delta t} + ze\frac{\delta C}{\delta t}$$

$$\frac{\delta \Omega}{\delta t} = \frac{\delta \omega}{\delta t} + zej$$

Local equilibrium:

$$s_{iK} = \frac{\partial W\left(\mathbf{F}, \tilde{\mathbf{D}}, C\right)}{\partial F_{iK}}, \quad \tilde{E}_K = \frac{\partial W\left(\mathbf{F}, \tilde{\mathbf{D}}, C\right)}{\partial \tilde{D}_K}, \quad \mu = ez\Phi + \frac{\partial W\left(\mathbf{F}, \tilde{\mathbf{D}}, C\right)}{\partial C}.$$

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

I think the theory formulated this way is consistent with the existing theories in the literature. By using a material description, the theory can be readily extended to including other effects, and can be readily used as a basis to formulate a finite element method. The remaining game is to specify $W\left(\mathbf{F}, \tilde{\mathbf{D}}, C\right)$ and $M\left(\mathbf{F}, \tilde{\mathbf{D}}, C\right)$.

References. I'm working in IFMA, France, and have three references with me. I have only studied the first two. I'll add more references later.

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