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VISCOELASTICITY AND POROELASTICITY IN ELASTOMERIC GELS**

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ABSTRACT An elastomeric gel is a mixture of a polymer network and a solvent. In response to changes in mechanical forces and in the chemical potential of the solvent in the environment, the gel evolves by two concurrent molecular processes: the conformational change of the network, and the migration of the solvent. The two processes result in viscoelasticity and poroelasticity, and are characterized by two material-specific properties: the time of viscoelastic relaxation and the effective diffusivity of the solvent through the network. The two properties define a material-specific length. The material-specific time and length enable us to discuss macroscopic observations made over different lengths and times, and identify limiting conditions in which viscoelastic and poroelastic relaxations have either completed or yet started. We formulate a model of homogeneous deformation, and use several examples to illustrate viscoelasticity-limited solvent migration, where the migration of the solvent is pronounced, but the size of the gel is so small that the rate of change is limited by viscoelasticity. We further describe a theory that evolves a gel through inhomogeneous states. Both infinitesimal and finite deformation are considered.

KEY WORDS elastomer, gel, viscoelasticity, poroelasticity, creep, stress relaxation

I. INTRODUCTION

Long and flexible polymer chains can be crosslinked to form a three-dimensional network, a single giant molecule commonly called an elastomer. When the network absorbs a species of small molecules (i.e., a solvent), the aggregate is known as an elastomeric gel. For example, a hydrogel is an aggregate of a polymer network and water molecules. Gels are being developed in diverse applications, such as vehicles for drug delivery[1,2], actuators and sensors in micro-devices[3–6], scaffolds in tissue engineering[7,8], and packers for enhanced oil recovery[9]. The deformation of gels is time-dependent, resulting from two concurrent molecular processes: the conformational change of the network, and the migration of the solvent (Fig.1). The two processes result in viscoelasticity and poroelasticity.

Concurrent viscoelasticity and poroelasticity have been observed in many materials. In geologic materials, viscoelasticity results from the sliding of the solid grains, and poroelasticity results from the migration of a liquid (e.g., water or oil)[10–14]. In living tissues and cells, viscoelasticity results from the conformational change of macromolecules, and poroelasticity results from the migration of

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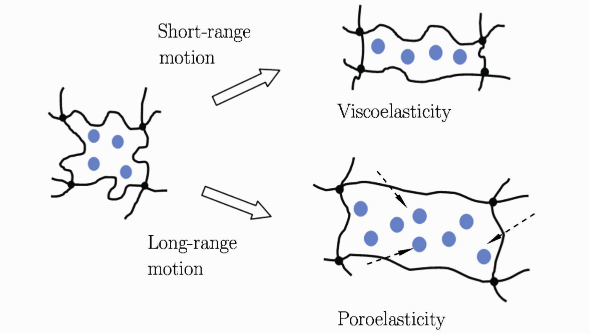


Fig. 1. A gel evolves by two molecular processes: the conformational change of the polymer network, and the migration of the solvent molecules. The two processes result in the macroscopic behavior of viscoelasticity and poroelasticity. In viscoelasticity, solvent molecules move relative to the polymer network over a short range. In poroelasticity, solvent molecules move relative to the polymer network over a long range.

small molecules[15–22]. A theory of poroviscoelasticity developed by Biot[23–25] has been used to analyze various phenomena[26–31].

The theory of poroviscoelasticity must be adapted for different classes of materials. Here we develop the theory to describe the concurrent viscoelasticity and poroelasticity of elastomeric gels. Our work has been motivated by a known challenge: concurrent viscoelasticity and poroelasticity makes the experimental characterization of materials extremely difficult[32–41]. It is of considerable practical value to identify conditions in which viscoelastic and poroelastic relaxations have either completed or yet started. We describe an approach and relate it to experimental observations. The time of viscoelastic relaxation and the effective diffusivity of solvent are material-specific properties. Together they define a material-specific length. Using the material-specific time and length, we classify macroscopic observations made over different lengths and times. We then formulate a model of homogeneous deformation, and use several examples to illustrate a particularly intriguing limiting case: viscoelasticity-limited solvent migration. We finally describe a theory that evolves a gel through a sequence of inhomogeneous fields. Both infinitesimal and finite deformation are considered.

II. TIME AND LENGTH

In an elastomeric gel, viscoelasticity results from molecular processes such as sliding between the polymer chains and rotation of the joints between the segments of an individual chain[42], so that the time of viscoelastic relaxation, τ_v, is independent of the length characteristic of any macroscopic observation[43]. By contrast, poroelasticity results from migration of the solvent, so that the time of poroelastic relaxation depends on the length of a macroscopic observation. Here the length of a macroscopic observation is referred to a representative geometric length in an experiment, which is much larger than the microscopic lengths such as the mesh size of a polymeric network and the size of solvent molecule. Examples of the macroscopic length include the sample size in a compression test, and the radius of contact in an indenta-

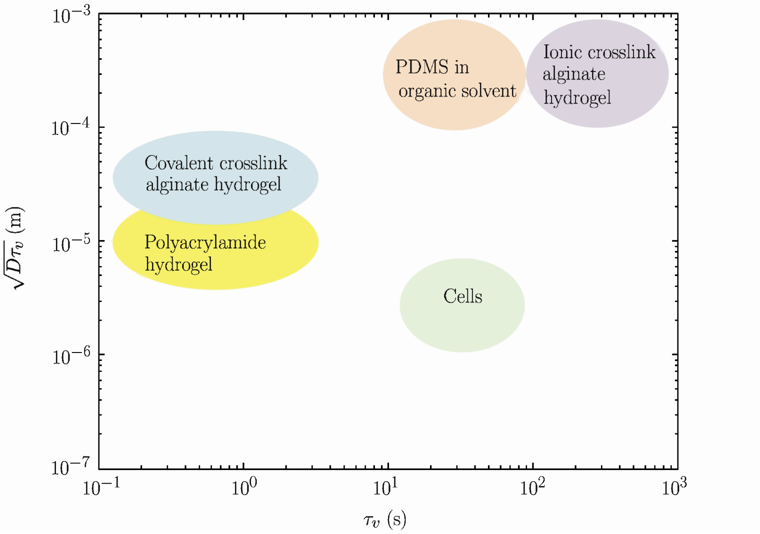


Fig. 2 Representative values of the viscoelastic relaxation time τ_v and the material-specific length $\sqrt{D\tau_v}$. The plot is intended to give a broad overview.

tion test. Poroelasticity is characterized by the effective diffusivity D of the solvent in the network. The two material-specific parameters define a length, $\sqrt{D\tau_v}$, which represents the distance of the spread of the solvent within a time comparable to the time of viscoelastic relaxation. The length $\sqrt{D\tau_v}$ is material-specific, and is independent of the length and time characteristic of any macroscopic observation. Values of the viscoelastic relaxation time τ_v and the material-specific length $\sqrt{D\tau_v}$ vary greatly among different materials. For a given polymer-solvent pair, the values of τ_v and $\sqrt{D\tau_v}$ also depend on the crosslink density of the polymer network, the concentration of the solvent; multiple times are also possible for different molecular processes of relaxation. Nonetheless, representative values of τ_v and $\sqrt{D\tau_v}$ should give a broad overview (Fig.2).

We next use the material-specific time τ_v and the material-specific length $\sqrt{D\tau_v}$ to discuss experimental observations made over a time t and a length L. Various limiting conditions can be represented graphically in a plane spanned by the normalized time and length of an observation (Fig.3). The condition $t \sim \tau_v$ represents the time of viscoelastic relaxation, and the condition $t \sim L^2/D$ represents the time and length of poroelastic relaxation. The two conditions divide the plane into four regions, each representing a condition of time-independent elasticity, where the viscoelastic and poroelastic relaxation have either completed or yet started. When $t << \tau_v$ and $t << L^2/D$, both processes have yet started, and the gel behaves like an elastic solid with unrelaxed moduli and with negligible migration of the solvent. When $t << \tau_v$ and $t >> L^2/D$, viscoelastic relaxation has yet started, but poroelastic relaxation has completed, and the gel behaves like an elastic solid with unrelaxed moduli and with pronounced migration of the solvent. When $t >> \tau_v$ and $t << L^2/D$, viscoelastic relaxation has completed, but poroelastic relaxation has yet started, and the gel behaves like an elastic solid with relaxed moduli and with negligible migration of the solvent. When $t >> \tau_v$ and $t >> L^2/D$, both processes are relaxed, and the gel behaves like an elastic solid with relaxed moduli and with pronounced migration of the solvent.

We can also use the approach to classify the time-dependent processes, which should occur under either the condition $t \sim \tau_v$ for viscoelastic relaxation or the condition $t \sim L^2/D$ for poroelastic relaxation. We first consider observations made over a large length, $L >> \sqrt{D\tau_v}$. When the time of observation is comparable to the time of poroelastic relaxation, $t \sim L^2/D$, we observe poroelastic relaxation, with elastic constants being those after viscoelastic relaxation. This case is illustrated by macro-scale indentation of gels[44–46]. The characteristic length of the experiment—the radius of contact—is on the order of 10^{-3} m. The measured relaxation time is on the order of hours. A typical value of the viscoelastic relaxation of covalently crosslinked gels is in seconds[47,48]. The experiment confirms a salient feature of poroelastic relaxation: the measured relaxation time scales with the square of the characteristic length of the experiment, the radius of contact. When the time of observation is comparable to the time of viscoelastic relaxation, $t \sim \tau_v$, poroelastic relaxation has yet started, and we observe viscoelastic relaxation. This case is illustrated by a compression test of a disk of alginate hydrogel[49]. The typical value of the diffusivity of alginate hydrogel is on the order of 10^{-9} m^2/s, and the characteristic length of the environment, the diameter of the disk is 10^{-2} m, so the time of poroelastic relaxation is on the order of 10^5 s. The measured relaxation time is on the order of 10^3 s. The experiment confirms a salient feature of viscoelastic relaxation: the measured relaxation time is independent of the diameter of the disk.

We next consider observations made over a small length, $L << \sqrt{D\tau_v}$. When the time of observation is comparable to the time of poroelastic relaxation, $t \sim L^2/D$, we observe poroelastic relaxation, with elastic constants being those before viscoelastic relaxation. When the time of observation is comparable to the time of viscoelastic relaxation, $t \sim \tau_v$, solvent has sufficient time to migrate over the length characteristic of the experiment, and we observe the relaxed poroelastic effect, along with viscoelastic relaxation. This case is illustrated by the experiments with cells and tissues tested by the atomic force microscopes and nanoindentation[50,51]. The radius of contact is small, say $10^{-5} \sim 10^{-6}$ m. A typical value of the effective diffusivity is $10^{-10} \sim 10^{-11}$ m^2/s, so that the time of poroelastic relaxation is on the order of $\tau_p = 10^{-2} \sim 10^0$ s. A typical value of the viscoelastic time of these materials is on the order of $\tau_v = 10 \sim 10^2$ s.

The above considerations are further illustrated by comparing two types of observations of living cells. Relaxation time of 10 s has been reported for both indentation of several micrometers[52], and compression of cell aggregates of hundreds of micrometers[53]. We interpret these observations as follows.

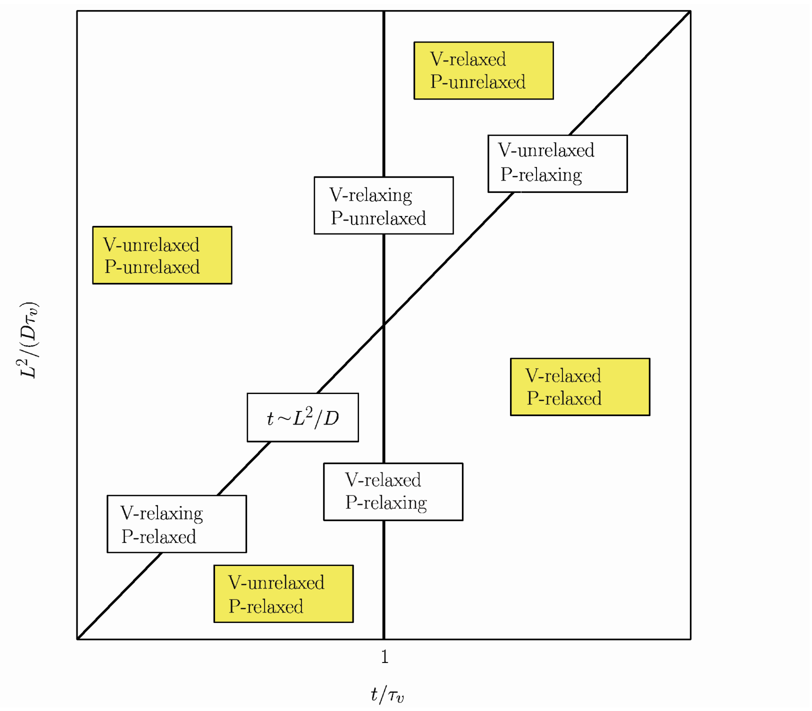


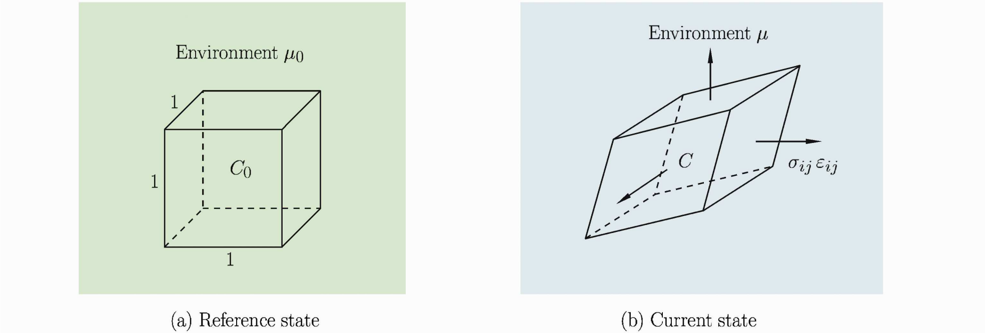
Fig. 3. A graphic representation of various limiting conditions. For a given material, the material-specific time τ_v and the material specific length $\sqrt{D\tau_v}$ are given, and each point in the plane corresponds to a time t and a length L of a macroscopic observation. The vertical line $t \sim \tau_v$ represents the time of viscoelastic relaxation, and the inclined line $t \sim L^2/D$ represents the time and length of poroelastic relaxation. For example, the lower part of the vertical line, marked as 'V-relaxing, P-relaxed', corresponding to the condition in which the migration of the solvent is pronounced, but the size of the gel is so small that the rate of change is limited by viscoelasticity. This condition, which we call viscoelasticity-limited migration of solvent, is analyzed in §IV. The two lines divide the plane into four regions, each representing a condition of time-independent elasticity, where the poroelastic and viscoelastic relaxation have either completed or yet started.

The effective diffusivity in the cells is $\sim 10^{-11}$ m^2/s[50,51]. The time of poroelastic relaxation over a length of micrometers is 10^{-1} s, and the time of poroelastic relaxation over a length of hundreds of micrometers is 10^3 s. In the first experiment, poroelastic relaxation happens much faster than viscoelastic relaxation. In the second experiment, the poroelastic relaxation happens much slower than viscoelastic relaxation. Both experiments give the time of viscoelastic relaxation.

III. HOMOGENEOUS STATES

Following a common practice in formulating a field theory, we regard a gel as a sum of many small pieces, and assume that each piece evolves in time through a sequence of homogenous states. Communication between the pieces is described by the kinematics of deformation, balance of forces, conservation of the solvent, and kinetics of the migration of the solvent. We will leave the communication between the pieces to §V, and focus this section on the homogeneous states of an individual small piece. To focus on essential ideas, we will devote most of the paper to infinitesimal deformation, with finite deformation discussed in §VI.

Consider a setup consisting of a gel, an environment, a set of forces, and a species of molecules—the solvent (Fig.4). Both the gel and the environment can contain more than one species of molecules, but the setup is such that the gel and the environment can exchange only one species of molecules: the solvent. The size of the gel is so small that migration of the solvent is fast relative to viscoelasticity. Consequently, the gel evolves by a sequence of homogeneous states. In the reference state, the gel is subject to no external forces, and is submerged in an environment in which the chemical potential of the solvent is fixed at μ_0. When the gel and the environment equilibrate, the gel is a unit cube containing C_0 number of solvent molecules. In the current state at time t, the gel is subject to a state of stress σ_{ij}, and is submerged in an environment in which the chemical potential of the solvent is fixed at a



(a) Reference state (b) Current state

Fig. 4. A gel is subject to stresses and submerged in an environment, and evolves through a sequence of homogeneous states. (a) In the reference state, subject to no stress and submerged in an environment in which the chemical potential of the solvent is μ_0, the gel is a unit cube and contains C_0 number of solvent molecules. (b) In the state at time t, subject to stress σ_{ij} and submerged in a solvent in which the chemical potential of solvent is μ, the gel deforms into a parallelepiped of strain ε_{ij} and contains C number of solvent molecules.

different value μ. Thus, σ_{ij} represents mechanical load, and $(\mu - \mu_0)$ represents chemical load. In the current state , the gel deforms into a parallelepiped of strain ε_{ij} relative to the cube, and contains C number of solvent molecules.

We regard the gel as a nonequilibrium thermodynamic system of seven external degrees of freedom, characterized by fourteen work-conjugate variables $(\varepsilon_{ij}, \sigma_{ij})$ and (C, μ). The evolution is taken to be isothermal, so that the temperature is not listed as a variable. Let W be the Helmholtz free energy of the gel in the current state minus the Helmholtz free energy of its constituents in the reference state—that is, the gel and $(C - C_0)$ number of solvent molecules in the reference state. The applied forces can be represented by hanging weights. When the parallelepiped deforms by a small amount $\delta\varepsilon_{ij}$, the potential energy of the weights change by $-\sigma_{ij}\delta\varepsilon_{ij}$. Associated with the transfer of δC number of solvent molecules from the environment to the gel, the Helmholtz free energy of the environment changes by $-(\mu - \mu_0)\,\delta C$.

The gel, the hanging weights and the environment together form a composite thermodynamic system. The composite exchanges energy by heat with a reservoir of energy held at a fixed temperature, but the composite receives neither work nor matter from the rest of the world. The Helmholtz free energy of the composite is the sum of the Helmholtz free energy of the gel, the potential energy of the weights, and the Helmholtz free energy of the environment. Thermodynamics requires that the change of the Helmholtz free energy of the composite should not increase:

$$\delta W - \sigma_{ij}\delta\varepsilon_{ij} - (\mu - \mu_0)\,\delta C \le 0 \tag{1}$$

The variation means the value of a quantity at a time minus that at a slightly earlier time. As usual in thermodynamics, this inequality involves the direction of time, but not the duration of time. The equality in (1) holds when the composite undergoes reversible changes around a state of equilibrium, and the inequality holds when the composite undergoes irreversible changes out of equilibrium.

We specify the changes of the system by a rheological model. The gel is a soft material, and is typically subject to a small stress. The individual polymer chains and solvent molecules are assumed to be incompressible[54]. The change in the volume of the gel is entirely due to the change in the number of solvent molecules in the gel:

$$\varepsilon_{kk} = \varOmega\,(C - C_0) \tag{2}$$

where $\varOmega$ is the volume per solvent molecule. Viscoelasticity is commonly pictured with arrangements of springs and dashpots[55]. To illustrate the procedure, we adopt a relatively simple spring-dashpot arrangement to represent elastomers (Fig.5)[56, 57]. The arrangement captures a salient feature of an elastomeric gel: the network is covalently crosslinked, so that the gel under a constant load will attain a state of equilibrium after viscoelastic relaxation. When the dashpot fully relaxes the stress in the spring β, the stress in the spring α will equilibrate with the applied load. The progression of viscoelastic relaxation is characterized by the strains of the dashpot, $\hat{\varepsilon}_{ij}$, which are the internal variables of the nonequilibrium thermodynamic system. The strain $\hat{\varepsilon}_{ij}$ of the dashpot and the strain ε_{ij} of the spring

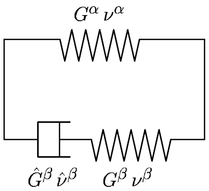


Fig. 5. A rheological model is represented by an arrangement of two springs and one dashpot. The spring α represents the elasticity of the gel after viscoelastic relaxation. The spring β and the dashpot represent viscoelastic relaxation.

α together fully specify a state of the system, and form a complete list of the independent variables of the Helmholtz free energy:

$$W = W\left(\varepsilon_{ij}, \hat{\varepsilon}_{ij}\right) \tag{3}$$

We have excluded C from the list of independent variables because C relates to strains by Eq.(2). According to differential calculus, when the independent variables change by $\delta\varepsilon_{ij}$ and $\delta\hat{\varepsilon}_{ij}$, the Helmholtz free energy changes by $\delta W = \left(\partial W/\partial\varepsilon_{ij}\right)\delta\varepsilon_{ij} + \left(\partial W/\partial\hat{\varepsilon}_{ij}\right)\delta\hat{\varepsilon}_{ij}$.

We next apply the thermodynamic inequality to the specific rheological model. Inserting Eqs.(2) and (3) into inequality (1), we obtain that

$$\left(\frac{\partial W}{\partial\varepsilon_{ij}} - \frac{\mu-\mu_0}{\varOmega}\delta_{ij} - \sigma_{ij}\right)\delta\varepsilon_{ij} + \frac{\partial W}{\partial\hat{\varepsilon}_{ij}}\delta\hat{\varepsilon}_{ij} \le 0 \tag{4}$$

This condition holds for arbitrary small changes $\delta\varepsilon_{ij}$ and $\delta\hat{\varepsilon}_{ij}$. Now consider the two types of changes separately. First, when the dashpot is constrained, $\delta\hat{\varepsilon}_{ij} = 0$, the two springs can still deform, $\delta\varepsilon_{ij} \neq 0$. The rheological model requires the two springs to equilibrate with the applied loads, and inequality (4) reduces to an equality for arbitrary small changes $\delta\varepsilon_{ij}$, giving that

$$\sigma_{ij} + \frac{\mu-\mu_0}{\varOmega}\delta_{ij} = \frac{\partial W}{\partial\varepsilon_{ij}} \tag{5}$$

Second, when the spring α is constrained, $\delta\varepsilon_{ij} = 0$, the system is no longer affected by the applied loads, but the spring β and the dashpot can still deform, $\delta\hat{\varepsilon}_{ij} \neq 0$. The rheological model requires the gel to dissipate energy, and inequality (4) reduces to an inequality for arbitrary small changes $\delta\hat{\varepsilon}_{ij}$:

$$\frac{\partial W}{\partial\hat{\varepsilon}_{ij}}\delta\hat{\varepsilon}_{ij} \le 0 \tag{6}$$

The equality (5) and the inequality (6) together fulfill the thermodynamic inequality (4) for arbitrary small changes $\delta\varepsilon_{ij}$ and $\delta\hat{\varepsilon}_{ij}$. Equality (5) is an equation of state: the stress and the chemical potential act together to deform the gel. Inequality (6) places a restriction on the kinetic model that describes how the gel dissipates energy by viscoelasticity.

The free energy of the gel is associated with the two springs in the rheological model (Fig.5). The strains of spring α are ε_{ij}, and the strains of spring β are $\varepsilon_{ij} - \hat{\varepsilon}_{ij}$. Both springs are taken to represent isotropic and linear elasticity, so that the Helmholtz free energy is quadratic in the strains:

$$W = G^\alpha\left[\varepsilon_{ij}\varepsilon_{ij} + \frac{\nu^\alpha}{1-2\nu^\alpha}\left(\varepsilon_{kk}\right)^2\right] + G^\beta\left[\left(\varepsilon_{ij}-\hat{\varepsilon}_{ij}\right)\left(\varepsilon_{ij}-\hat{\varepsilon}_{ij}\right) + \frac{\nu^\beta}{1-2\nu^\beta}\left(\varepsilon_{kk}-\hat{\varepsilon}_{kk}\right)^2\right] \tag{7}$$

where G^α and G^β are the shear moduli of the two springs, and ν^α and ν^β are Poisson's ratio.

Inserting this free-energy function into Eq.(5), we obtain that

$$\sigma_{ij} + \frac{\mu-\mu_0}{\varOmega}\delta_{ij} = 2G^\alpha\left[\varepsilon_{ij} + \frac{\nu^\alpha}{1-2\nu^\alpha}\varepsilon_{kk}\delta_{ij}\right] + 2G^\beta\left[\left(\varepsilon_{ij}-\hat{\varepsilon}_{ij}\right) + \frac{\nu^\beta}{1-2\nu^\beta}\left(\varepsilon_{kk}-\hat{\varepsilon}_{kk}\right)\delta_{ij}\right] \tag{8}$$

The two terms on the right-hand side represent the stresses in the two springs. Because the springs are parallel in the rheological model, the sum of the stresses in the two springs balances the applied stresses and the change in the chemical potential of the solvent in the environment. The change in the chemical potential is equivalent to a hydrostatic stress. The motion of the dashpot regulates the relaxation of the stresses in the spring β. When the spring β is unrelaxed, $\hat{\varepsilon}_{ij} \neq 0$ and both springs carry stresses. When the spring β is relaxed, $\hat{\varepsilon}_{ij} = \varepsilon_{ij}$, and only the spring α carry stresses. Assumption Eq.(2) relates the volumetric strain to the number of solvent molecules absorbed. When the number of solvent molecules in the gel is fixed, $C = C_0$, the volumetric strains vanish, $\varepsilon_{kk} = \hat{\varepsilon}_{kk} = 0$, and Eq.(8) characterizes an incompressible material. When the number of solvent molecules changes, Eq.(8) characterizes a compressible material. Poisson's ratios ν^α and ν^β are dimensionless measures of the ability of the gel to exchange solvent with the environment. When $\nu^\alpha = \nu^\beta = 1/2$, the gel cannot exchange solvent with the environment. When $-1 < \nu^\alpha < 1/2$ and $-1 < \nu^\beta < 1/2$, the gel can exchange solvent with the environment.

The inequality (6) is satisfied by specifying a kinetic model for the dashpot. The stresses on the dashpot are

$$\sigma_{ij}^\beta = 2G^\beta \left[(\varepsilon_{ij} - \hat{\varepsilon}_{ij}) + \frac{\nu^\beta}{1-2\nu^\beta} (\varepsilon_{kk} - \hat{\varepsilon}_{kk}) \delta_{ij} \right] \tag{9}$$

Note that $\sigma_{ij}^\beta = -\partial W / \partial \hat{\varepsilon}_{ij}$. We model the dashpot as an isotropic, linearly viscous material—that is, the rate of deformation, $\partial \hat{\varepsilon}_{ij} / \partial t$, relates to the stress as

$$\frac{\partial \hat{\varepsilon}_{ij}}{\partial t} = \frac{1}{2\hat{G}^\beta} \left(\sigma_{ij}^\beta - \frac{\hat{\nu}^\beta}{1+\hat{\nu}^\beta} \sigma_{kk}^\beta \delta_{ij} \right) \tag{10}$$

where $\hat{G}^\beta$ and $\hat{\nu}^\beta$ are the constants that specify the viscous behavior of the dashpot. The inequality (6) is satisfied by setting $\hat{G}^\beta > 0$ and $-1 < \hat{\nu}^\beta < 1/2$. For an incompressible Newtonian fluid, $\hat{G}^\beta$ is the viscosity and $\hat{\nu}^\beta \to 1/2$. During the swelling of a gel, however, the polymer network must deform, which will cause viscoelasticity, so that $\hat{\nu}^\beta < 1/2$. A combination of Eqs.(9) and (10) gives

$$\frac{\partial \hat{\varepsilon}_{ij}}{\partial t} = \frac{G^\beta}{\hat{G}^\beta} \left[(\varepsilon_{ij} - \hat{\varepsilon}_{ij}) + \frac{\nu^\beta - \hat{\nu}^\beta}{(1-2\nu^\beta)(1+\hat{\nu}^\beta)} (\varepsilon_{kk} - \hat{\varepsilon}_{kk}) \delta_{ij} \right] \tag{11}$$

The pre-factor defines a time scale of viscoelastic relaxation: $\tau_v = \hat{G}^\beta / G^\beta$. This time scale can be modified by using dimensionless parameters ν^α, ν^β, $\hat{\nu}^\beta$, and G^β / G^α. Specific times of viscoelastic deformation will be discussed later.

The model of homogeneous states can be summarized as follows. The gel is modeled as a nonequilibrium thermodynamic system of seven external degrees of freedom, characterized by the fourteen work-conjugate variables $(\varepsilon_{ij}, \sigma_{ij})$ and (C, μ). To fully characterize a state of the gel, we further specify six internal variables—the strains of the dashpot, $\hat{\varepsilon}_{ij}$. The system is governed by the seven equations of state (2) and (8), and six kinetic equation (11). These equations couple the external and internal variables. To evolve the state of the gel, we can independently prescribe any seven of the fourteen external variables as functions of time, and use the seven equations of state and the six kinetic equations to evolve the other seven external variables in time, along with the six internal variables.

The algebra of the model becomes more transparent if we separate volumetric and deviatoric components. Define the mean stress as $\sigma_m = \sigma_{kk}/3$, the deviatoric stresses as $s_{ij} = \sigma_{ij} - \sigma_m \delta_{ij}$, the volumetric strain as ε_{kk}, the deviatoric strains as $e_{ij} = \varepsilon_{ij} - \varepsilon_{kk}\delta_{ij}/3$, the volumetric strain of the dashpot as $\hat{\varepsilon}_{kk}$, and the deviatoric strains of the dashpot as $\hat{e}_{ij} = \hat{\varepsilon}_{ij} - \hat{\varepsilon}_{kk}\delta_{ij}/3$. The equations of state (8) take the form

$$s_{ij} = 2G^\alpha e_{ij} + 2G^\beta (e_{ij} - \hat{e}_{ij}), \qquad \sigma_m + \frac{\mu - \mu_0}{\Omega} = K^\alpha \varepsilon_{kk} + K^\beta (\varepsilon_{kk} - \hat{\varepsilon}_{kk}) \tag{12}$$

where $K^\alpha = 2G^\alpha (1+\nu^\alpha) / [3(1-2\nu^\alpha)]$ and $K^\beta = 2G^\beta \left(1+\nu^\beta\right) / \left[3\left(1-2\nu^\beta\right)\right]$ are the bulk moduli of the two springs. Recall that assumption Eq.(2) relates the volumetric strain to the number of solvent molecules absorbed. The two bulk moduli measure the ability of the gel to exchange the solvent with the environment. The kinetic model (11) becomes

$$\frac{\partial \hat{e}_{ij}}{\partial t} = \frac{G^\beta}{\hat{G}^\beta} (e_{ij} - \hat{e}_{ij}), \qquad \frac{\partial \hat{\varepsilon}_{kk}}{\partial t} = \frac{K^\beta}{\hat{K}^\beta} (\varepsilon_{kk} - \hat{\varepsilon}_{kk}) \tag{13}$$

where $\hat{K}^\beta = 2\hat{G}^\beta \left(1+\hat{\nu}^\beta\right) / \left[3\left(1-2\hat{\nu}^\beta\right)\right]$ is the bulk viscosity of the dashpot. When the network absorbs the solvent and swells, the polymer chains are stretched. The viscoelasticity associated with volumetric deformation is characterized by the bulk modulus K^{β} and the bulk viscosity $\hat{K}^{\beta}$. When a state of strain ε_{ij} is suddenly prescribed and is subsequently held constant, strains of dashpot evolve according to Eq.(13), and the stresses relax according to Eq.(12). The volumetric and deviatoric components relax over two distinct times, $\hat{G}^{\beta}/G^{\beta}$ and $\hat{K}^{\beta}/K^{\beta}$, respectively.

From Eq.(12) we can solve for strains

$$e_{ij} = \frac{1}{G^{\alpha}+G^{\beta}}\left(\frac{s_{ij}}{2}+G^{\beta}\hat{e}_{ij}\right), \qquad \varepsilon_{kk} = \frac{1}{K^{\alpha}+K^{\beta}}\left(\sigma_m+\frac{\mu-\mu_0}{\Omega}+K^{\beta}\hat{\varepsilon}_{kk}\right) \tag{14}$$

We can also eliminate the strains from Eqs.(12) and (13), so that

$$\frac{\partial \hat{e}_{ij}}{\partial t} = \frac{G^{\beta}}{\hat{G}^{\beta}\left(G^{\alpha}+G^{\beta}\right)}\left(\frac{s_{ij}}{2}-G^{\alpha}\hat{e}_{ij}\right), \quad \frac{\partial \hat{\varepsilon}_{kk}}{\partial t} = \frac{K^{\beta}}{\hat{K}^{\beta}\left(K^{\alpha}+K^{\beta}\right)}\left(\sigma_m+\frac{\mu-\mu_0}{\Omega}-K^{\alpha}\hat{\varepsilon}_{kk}\right) \tag{15}$$

Equations (14) and (15) are convenient when the stresses and chemical potential are prescribed. When a state of stress σ_{ij} is suddenly prescribed and is subsequently held constant, strains of dashpot evolve according to Eq.(15), and the stresses creep according to Eq.(12). The volumetric and deviatoric components creep over two distinct times, $\hat{G}^{\beta}\left(G^{\alpha}+G^{\beta}\right)/\left(G^{\alpha}G^{\beta}\right)$ and $\hat{K}^{\beta}\left(K^{\alpha}+K^{\beta}\right)/\left(K^{\alpha}K^{\beta}\right)$, respectively. These times of creep are longer than those of stress relaxation.

IV. VISCOELASTICITY-LIMITED SOLVENT MIGRATION

This section focuses on observations made over a small length, and over a time comparable to the time of viscoelastic relaxation. As mentioned in §II, the viscoelasticity-limited solvent migration is of particular interest for experimental observations of small lengths. In this section the viscoelasticity-limited migration is considered in its simplest form: a gel in a homogeneous state, subject to stresses and submerged in an environment. The size of the gel is so small that the gel and the environment exchanges solvent readily within the time of viscoelastic relaxation.

4.1. Blocking Force Generated by an Environmental Change

As a first example, consider a gel confined in a rigid box, so that $\varepsilon_{ij} = 0$. The box, however, is permeable to the solvent. When the chemical potential of the solvent in the environment increases from μ_0 to μ, the number of solvent molecules in the gel remains to be C_0, but the gel develops a state of stress. In the short-time limit, the dashpot has not moved, $\hat{\varepsilon}_{ij}(0) = 0$. The kinetic model (13) indicates that strain of the dashpot will be zero at all time, $\hat{\varepsilon}_{ij}(t) = 0$. Equations of state (12) give the stresses

$$\sigma_{11} = \sigma_{22} = \sigma_{33} = -\frac{\mu-\mu_0}{\Omega} \tag{16}$$

When the gel is confined in the rigid and porous box, the change in the chemical potential generates a state of hydrostatic stress.

When the gel is constrained and cannot deform, our model predicts that the gel develops the stress Eq.(16) instantaneously when the chemical potential of the solvent in the environment changes. This puzzling prediction is caused by the assumption of molecular incompressibility Eq.(2). In reality, the molecules do compress somewhat when the number of molecules is fixed. Consequently, when the chemical potential of the solvent in the environment is increased, some molecules will migrate into the gel, and the volume needed is accommodated by the bulk elasticity. The time for relaxation will be inversely proportional to the elastic bulk modulus, which we have tacitly assumed to be infinite by invoking the assumption of molecular incompressibility Eq.(2).

4.2. Free Swelling in Response to an Environmental Change

In this example, the gel has been in equilibrium with an environment in which the chemical potential of the solvent is μ_0, and is suddenly switched into a new environment in which the chemical potential of the solvent is of a higher value μ. The gel is subject to no applied stresses, $\sigma_{ij} = 0$, and swells freely by absorbing more solvent. The swelling is isotropic: all the shear strains vanish, and the normal strains are isotropic, $\varepsilon_{11} = \varepsilon_{22} = \varepsilon_{33}$ and $\hat{\varepsilon}_{11} = \hat{\varepsilon}_{22} = \hat{\varepsilon}_{33}$. The kinetic model (15) reduces to

$$\frac{\partial \hat{\varepsilon}_{kk}}{\partial t} = \frac{K^{\beta}}{\hat{K}^{\beta}\left(K^{\alpha}+K^{\beta}\right)}\left(\frac{\mu-\mu_0}{\Omega}-K^{\alpha}\hat{\varepsilon}_{kk}\right) \tag{17}$$

In the short-time limit, the dashpot has not moved, $\hat{\varepsilon}_{kk}(0) = 0$. The ordinary differential equations (17) gives the solution:

$$\hat{\varepsilon}_{kk}(t) = \frac{(\mu - \mu_0)}{K^\alpha \Omega} \left\{ 1 - \exp\left[-\frac{K^\alpha K^\beta t}{(K^\alpha + K^\beta) \hat{K}^\beta} \right] \right\} \tag{18}$$

Inserting Eq.(18) into Eq.(14), we obtain that

$$\varepsilon_{kk}(t) = \frac{(\mu - \mu_0)}{K^\alpha \Omega} - \frac{K^\beta (\mu - \mu_0)}{K^\alpha (K^\alpha + K^\beta) \Omega} \exp\left[-\frac{K^\alpha K^\beta t}{(K^\alpha + K^\beta) \hat{K}^\beta} \right] \tag{19}$$

The amount of swelling ε_{kk} is proportional to the change in the chemical potential, and increases in time as the gel undergoes viscoelastic creep. In the short-time limit, $\varepsilon_{kk}(0) = (\mu - \mu_0) / \left[\Omega \left(K^\alpha + K^\beta\right)\right]$, and the amount of swelling is inversely proportional to the combined bulk moduli of the two springs. In the long time limit, $\varepsilon_{kk}(\infty) = (\mu - \mu_0)/(\Omega K^\alpha)$, the stress in the spring β is fully relaxed, and the amount of swelling is inversely proportional to the bulk modulus of the spring α.

4.3. Creep under a Uniaxial Force

This example analyzes the commonly performed creep test. The gel is immersed in an environment in which the chemical potential of the solvent is fixed at μ_0. The gel is compressed between two rigid plates. Then a dead load is suddenly placed on the gel, and the stress σ_{33} is maintained as a constant level subsequently. The gel is slippery so that the plates do not cause any lateral stress in the gel, $\sigma_{11} = \sigma_{22} = 0$. The plates are porous so that the gel and the environment can exchange solvent. We are interested in the evolution of the strains $\varepsilon_{11}(t)$ and $\varepsilon_{33}(t)$. The mean stress is $\sigma_m = \sigma_{33}/3$, and the deviatoric stresses are $s_{11} = s_{22} = -\sigma_{33}/3$ and $s_{33} = 2\sigma_{33}/3$. The kinetic model (15) reduces to

$$\begin{aligned}
\frac{\partial \hat{e}_{11}}{\partial t} &= \frac{G^\beta}{\hat{G}^\beta (G^\alpha + G^\beta)} \left(-\frac{\sigma_{33}}{6} - G^\alpha \hat{e}_{11} \right) \\
\frac{\partial \hat{e}_{33}}{\partial t} &= \frac{G^\beta}{\hat{G}^\beta (G^\alpha + G^\beta)} \left(\frac{\sigma_{33}}{3} - G^\alpha \hat{e}_{11} \right) \\
\frac{\partial \hat{\varepsilon}_{kk}}{\partial t} &= \frac{K^\beta}{\hat{K}^\beta (K^\alpha + K^\beta)} \left(\frac{\sigma_{33}}{3} - K^\alpha \hat{\varepsilon}_{kk} \right)
\end{aligned} \tag{20}$$

At time zero, the dashpot has not moved, $\hat{e}_{11}(0) = \hat{e}_{33}(0) = \hat{\varepsilon}_{33}(0) = 0$. The three ordinary differential equations yield solutions:

$$\begin{aligned}
\hat{e}_{11}(t) &= -\frac{\sigma_{33}}{6G^\alpha} \left\{ 1 - \exp\left[-\frac{G^\beta G^\alpha t}{\hat{G}^\beta (G^\alpha + G^\beta)} \right] \right\} \\
\hat{e}_{33}(t) &= \frac{\sigma_{33}}{3G^\alpha} \left\{ 1 - \exp\left[-\frac{G^\beta G^\alpha t}{\hat{G}^\beta (G^\alpha + G^\beta)} \right]) \right\} \\
\hat{\varepsilon}_{33}(t) &= \frac{\sigma_{33}}{3K^\alpha} \left\{ 1 - \exp\left[-\frac{K^\alpha K^\beta t}{\hat{K}^\beta (K^\alpha + K^\beta)} \right] \right\}
\end{aligned} \tag{21}$$

Inserting Eq.(21) into Eq.(14), we obtain that

$$\begin{aligned}
\varepsilon_{11}(t) = &-\frac{\sigma_{33}}{6G^\alpha} + \frac{\sigma_{33}}{9K^\alpha} + \frac{\sigma_{33} G^\beta}{6G^\alpha (G^\alpha + G^\beta)} \exp\left[-\frac{G^\beta G^\alpha t}{\hat{G}^\beta (G^\alpha + G^\beta)} \right] \\
&- \frac{\sigma_{33} K^\beta}{9K^\alpha (K^\alpha + K^\beta)} \exp\left[-\frac{K^\beta K^\alpha t}{\hat{K}^\beta (K^\alpha + K^\beta)} \right] \\
\varepsilon_{33}(t) = &\frac{\sigma_{33}}{3G^\alpha} + \frac{\sigma_{33}}{9K^\alpha} - \frac{\sigma_{33} G^\beta}{3G^\alpha (G^\alpha + G^\beta)} \exp\left[-\frac{G^\beta G^\alpha t}{\hat{G}^\beta (G^\alpha + G^\beta)} \right] \\
&- \frac{\sigma_{33} K^\beta}{9K^\alpha (K^\alpha + K^\beta)} \exp\left[-\frac{K^\beta K^\alpha t}{\hat{K}^\beta (K^\alpha + K^\beta)} \right]
\end{aligned} \tag{22}$$

The strains creep over two times, $\hat{G}^{\beta}\left(G^{\alpha}+G^{\beta}\right)/\left(G^{\alpha}G^{\beta}\right)$ and $\hat{K}^{\beta}\left(K^{\alpha}+K^{\beta}\right)/\left(K^{\alpha}K^{\beta}\right)$, one for the deviatoric components, and the other for the volumetric components. If the two times are very different, the strain-time curves will show two plateaus.

4.4. Constrained Swelling in Response to an Environmental Change

To avoid mathematical complications, in each example above we prescribe either all components of the strain, or all components of the stress (including the chemical potential). As noted in §III, for such an example, the deviatoric and volumetric components evolve independently, each with its own characteristic time. For many other phenomena, however, a mixture of certain components of the stress and of the strain are prescribed, so that we have to solve for the other components of the strain from the equations of state (8), and then substitute into the kinetic equation (11), resulting in a set of coupled ordinary differential equations for $\hat{\varepsilon}_{ij}$.

As an example, consider a thin layer of a gel bonded to a rigid substrate. Before time zero, the gel is in equilibrium with an environment in which the chemical potential of the solvent is μ_0. At time zero, the gel is switched into a new environment in which the chemical potential of the solvent is fixed at a higher value, μ. We are interested in the swelling of the gel under the constraint of the substrate. In this example, all shear components of the stress and the strain vanish. Prescribed are the chemical potential μ, the stress normal to the layer $\sigma_{33}=0$, and the lateral strains $\varepsilon_{11}=\varepsilon_{22}=0$. To be determined are the strain normal to the layer $\varepsilon_{33}(t)$, the lateral stresses $\sigma_{11}(t)=\sigma_{22}(t)$, and the strains of the dashpot $\hat{\varepsilon}_{11}(t)=\hat{\varepsilon}_{22}(t)$ and $\hat{\varepsilon}_{33}(t)$. In this example, because a mixture of stresses and strains are prescribed, the separation of deviatoric and volumetric components does not simplify the algebra. We will use Eqs.(8) and (11) instead. The equations of state (8) reduce to

$$\sigma_{11}=\frac{2\nu^{\alpha}G^{\alpha}}{1-2\nu^{\alpha}}\varepsilon_{33}+\frac{2G^{\beta}}{1-2\nu^{\beta}}\left[-\hat{\varepsilon}_{11}+\nu^{\beta}\left(\varepsilon_{33}-\hat{\varepsilon}_{33}\right)\right] \tag{23}$$

$$\frac{\mu-\mu_0}{\Omega}=\frac{2\left(1-\nu^{\alpha}\right)G^{\alpha}}{1-2\nu^{\alpha}}\varepsilon_{33}+\frac{2G^{\beta}}{1-2\nu^{\beta}}\left[\left(1-\nu^{\beta}\right)\left(\varepsilon_{33}-\hat{\varepsilon}_{33}\right)-2\nu^{\beta}\hat{\varepsilon}_{11}\right] \tag{24}$$

In the short-time limit, the dashpot is immobile, $\hat{\varepsilon}_{11}(0)=\hat{\varepsilon}_{33}(0)=0$, the two springs carry the applied stress σ_{33} in parallel, and Eqs.(23) and (24) give that

$$\varepsilon_{33}(0)=\frac{1}{2\left(1-\nu^{\alpha}\right)G^{\alpha}/(1-2\nu^{\alpha})+2\left(1-\nu^{\beta}\right)G^{\beta}/(1-2\nu^{\beta})}\left(\frac{\mu-\mu_0}{\Omega}\right) \tag{25}$$

$$\sigma_{11}(0)=\frac{\nu^{\alpha}G^{\alpha}/(1-2\nu^{\alpha})+\nu^{\beta}G^{\beta}/(1-2\nu^{\beta})}{\left(1-\nu^{\alpha}\right)G^{\alpha}/(1-2\nu^{\alpha})+\left(1-\nu^{\beta}\right)G^{\beta}/(1-2\nu^{\beta})}\left(\frac{\mu-\mu_0}{\Omega}\right) \tag{26}$$

In the long-time limit, the stress in the spring β is fully relaxed $\hat{\varepsilon}_{11}(\infty)\to 0$ and $\hat{\varepsilon}_{33}(\infty)\to\varepsilon_{33}(\infty)$, only spring α carries the applied stress, and Eqs.(23) and (24) give that

$$\varepsilon_{33}(\infty)=\frac{1-2\nu^{\alpha}}{2\left(1-\nu^{\alpha}\right)G^{\alpha}}\left(\frac{\mu-\mu_0}{\Omega}\right) \tag{27}$$

$$\sigma_{11}(\infty)=\frac{\nu^{\alpha}}{1-\nu^{\alpha}}\left(\frac{\mu-\mu_0}{\Omega}\right) \tag{28}$$

Equation (27) gives the amount of swelling of the gel under the constraint, which can be compared with the amount of swelling of the gel under no constraint, $\varepsilon_{kk}(\infty)=(\mu-\mu_0)/(\Omega K^{\alpha})$. Their ratio is $(1+\nu^{\alpha})/[3(1-\nu^{\alpha})]$. Assuming $-1<\nu^{\alpha}<1/2$, we note that $(1+\nu^{\alpha})/[3(1-\nu^{\alpha})]<1$. As expected, the gel under the constraint swells less that the gel under no constraint.

To study the evolution of the gel in time, we specialize the kinetic equation (11) as

$$\frac{\partial\hat{\varepsilon}_{11}}{\partial t}=\frac{G^{\beta}}{\hat{G}^{\beta}\left(1-2\nu^{\beta}\right)\left(1+\hat{\nu}^{\beta}\right)}\left[\left(\nu^{\beta}-\hat{\nu}^{\beta}\right)\left(\varepsilon_{33}-\hat{\varepsilon}_{33}\right)-\left(1-\hat{\nu}^{\beta}-2\nu^{\beta}\hat{\nu}^{\beta}\right)\hat{\varepsilon}_{11}\right] \tag{29}$$

$$\frac{\partial\hat{\varepsilon}_{33}}{\partial t}=\frac{G^{\beta}}{\hat{G}^{\beta}\left(1-2\nu^{\beta}\right)\left(1+\hat{\nu}^{\beta}\right)}\left[\left(1-\nu^{\beta}-2\nu^{\beta}\hat{\nu}^{\beta}\right)\left(\varepsilon_{33}-\hat{\varepsilon}_{33}\right)-2\left(\nu^{\beta}-\hat{\nu}^{\beta}\right)\hat{\varepsilon}_{11}\right] \tag{30}$$

From Eq.(22) we expressε_{33} in terms of the chemical potential and the strains of the dashpot:

$$\varepsilon_{33} = \frac{\mu - \mu_0/\Omega + 2G^\beta/(1-2\nu^\beta)\left[\left(1-\nu^\beta\right)\hat{\varepsilon}_{33} + 2\nu^\beta\hat{\varepsilon}_{11}\right]}{2\left(1-\nu^\alpha\right)G^\alpha/(1-2\nu^\alpha) + 2\left(1-\nu^\beta\right)G^\beta/(1-2\nu^\beta)} \tag{31}$$

Substituting Eq.(31) into Eqs.(29) and (30), we obtain two coupled ordinary differential equations for $\hat{\varepsilon}_{11}(t)$ and $\hat{\varepsilon}_{33}(t)$. The gel creeps over two times scales, which are different from those identified so far, and can be determined by solving an eigenvalue problem associated with Eqs.(29) and (30). The algebra is lengthy and not particularly illuminating, and is neglected here.

V. INHOMOGENEOUS STATES

This section formulates the theory that evolves a gel by inhomogeneous states (Fig.6). As mentioned before, we regard the gel as a sum of many small pieces, and assume that each piece evolves in time through homogeneous states, as governed by the equations of state (2) and (8), as well as the kinetic equation (11). This section adds the communication between the pieces: the kinematics of deformation, balance of forces, conservation of the solvent, and kinetics of the migration of the solvent.

We label each small piece of the gel by the coordinate of the piece, $\boldsymbol{x}$. Let $u_i(\boldsymbol{x},t)$ be the displacement of the piece at time t. The field of strain is defined as usual:

$$\varepsilon_{ij} = \frac{u_{i,j} + u_{j,i}}{2} \tag{32}$$

Let $\sigma_{ij}(\boldsymbol{x},t)$ be the stresses acting on the piece at $\boldsymbol{x}$ at time t. The balance of forces requires that

$$\sigma_{ij,j} = 0 \tag{33}$$

Let $C(\boldsymbol{x},t)$ be the concentration (i.e., the number of solvent molecules in a small piece of the gel divided by the volume of the piece). Let $J_k(\boldsymbol{x},t)$ be the flux of the solvent (i.e., the number of solvent molecules across a unit area per unit time). The conservation of the number of solvent molecules requires that

$$\frac{\partial C}{\partial t} + J_{k,k} = 0 \tag{34}$$

For each small piece of the gel, the surround gel serves as a solvent-containing environment. Let $\mu(\boldsymbol{x},t)$ be the chemical potential of the solvent. We relate the flux to the gradient of the chemical potential by using a kinetic model similar to Darcy's law:

$$J_i = -\left(\frac{\kappa}{\eta\Omega^2}\right)\mu_{,i} \tag{35}$$

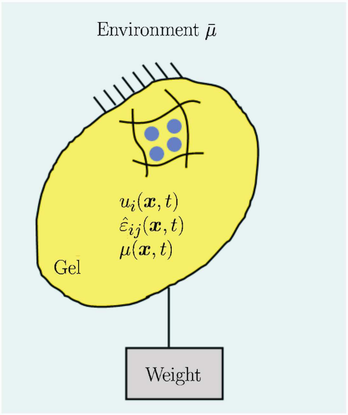


Fig. 6. A body of a gel is subject to mechanical forces and submerged in an environment, in which the chemical potential of the solvent is $\bar{\mu}$. Each small piece of the gel is marked by the coordinate $\boldsymbol{x}$. The state of the gel is characterized by ten time-dependent fields: the displacement $u_i(\boldsymbol{x},t)$, the chemical potential of the solvent $\mu(\boldsymbol{x},t)$, and the strain of the dashpot, $\hat{\varepsilon}_{ij}(\boldsymbol{x},t)$. The gel evolves through a sequence of inhomogeneous states.

where κ is the permeability of the gel which has the dimension of length squared, and η is the viscosity of the solvent. The negative sign indicates that the solvent flows from a piece of high chemical potential to a piece of low chemical potential.

The above equations specify the physical ingredients of the theory that evolve a gel through a sequence of inhomogeneous states. We can readily confirm that the theory satisfies the thermodynamic inequality. Let the traction be T_i; the balance of forces requires that $\sigma_{ij}n_j = T_i$, where n_j is the unit vector normal to the surface. The applied forces can be represented by hanging weights. When the surface of the gel moves at velocity $\partial u_i/\partial t$, the potential energy of the weights per unit time changes by $-\int T_i\left(\partial u_i/\partial t\right)\mathrm{d}A$. The gel is immersed in an environment in which the chemical potential of the solvent is $\bar{\mu}$. At the surface of the gel in contact with the environment, the gel is locally in equilibrium with the environment, $\mu = \bar{\mu}$. Associated with the transfer of the flux J_i, the Helmholtz free energy of the environment changes per unit time by $+\int\left(\bar{\mu}-\mu_0\right)J_i n_i = \mathrm{d}A$. Here the positive sign conforms to the convention that n_j is directed from the gel to the environment, and that $J_i n_i$ is the number of solvent molecules flowing out of the gel and into the environment per unit area and per unit time. The gel, the hanging weights and the environment together form a composite thermodynamic system. Thermodynamics requires that no process should increase the Helmholtz free energy of the composite:

$$\int \frac{\delta W}{\delta t}\mathrm{d}V + \int\left(\bar{\mu}-\mu_0\right)J_i n_i \mathrm{d}A - \int T_i \frac{\partial u_i}{\partial t}\mathrm{d}A \le 0 \tag{36}$$

The equality holds when the process is reversible and the inequality holds when the process is irreversible. Recall from §III that $\delta W = \left(\partial W/\partial \varepsilon_{ij}\right)\delta\varepsilon_{ij} + \left(\partial W/\partial \hat{\varepsilon}_{ij}\right)\delta\hat{\varepsilon}_{ij}$, $\varepsilon_{kk} = \Omega\left(C - C_0\right)$ and $\partial W/\partial \varepsilon_{ij} = \sigma_{ij} + \delta_{ij}\left(\mu-\mu_0\right)/\Omega$. Inequality (32) becomes

$$\int \frac{\partial W}{\partial \hat{\varepsilon}_{ij}}\frac{\delta \hat{\varepsilon}_{ij}}{\delta t}\mathrm{d}V + \int J_k \mu_{,k}\mathrm{d}V \le 0 \tag{37}$$

In reaching Eq.(37), we have used Eqs.(5), (33)-(35) and the theorem of divergence. The derivation of Eq.(37) is general and independent of the specific form of the kinetic models. The inequality describes that the system dissipates energy in two ways: local viscoelasticity of the polymer chains and long-rang migration of the solvent. For example, the thermodynamic inequality (37) is satisfied by the two kinetic models: the viscous model (10) and Darcy's law (35).

The theory can be represented as a set of differential equations for ten functions: $u_i(\boldsymbol{x},t)$, $\mu(\boldsymbol{x},t)$ and $\hat{\varepsilon}_{ij}(\boldsymbol{x},t)$. A combination of Eqs.(8), (33) and (34) gives that

$$G^{\alpha}\left(u_{i,jj} + \frac{1}{1-2\nu^{\alpha}}u_{k,ki}\right) + G^{\beta}\left(u_{i,jj} + \frac{1}{1-2\nu^{\beta}}u_{k,ki}\right) = \frac{\mu_{,i}}{\Omega} + 2G^{\beta}\left(\hat{\varepsilon}_{ij,j} + \frac{\nu^{\beta}}{1-2\nu^{\beta}}\hat{\varepsilon}_{kk,i}\right) \tag{38}$$

A combination of Eqs.(2), (28), (30) and (31) gives that

$$\frac{\partial u_{k,k}}{\partial t} = \frac{\kappa}{\eta\Omega}\mu_{,kk} \tag{39}$$

A combination of Eqs.(11) and (28) gives that

$$\frac{\partial \hat{\varepsilon}_{ij}}{\partial t} = \frac{G^{\beta}}{\eta^{\beta}}\left[\left(u_{i,j} - \hat{\varepsilon}_{ij}\right) + \frac{\nu^{\beta} - \hat{\nu}^{\beta}}{\left(1-2\nu^{\beta}\right)\left(1+\hat{\nu}^{\beta}\right)}\left(u_{k,k} - \hat{\varepsilon}_{kk}\right)\delta_{ij}\right] \tag{40}$$

Equations (38)-(40) constitute ten partial differential equations that, together with boundary and initial conditions, evolve the ten fields $u_i(\boldsymbol{x},t)$, $\mu(\boldsymbol{x},t)$ and $\hat{\varepsilon}_{ij}(\boldsymbol{x},t)$.

Eliminating the chemical potential by combining Eqs.(38) and (39), and recalling Eq.(2), we obtain that

$$\frac{\partial C}{\partial t} = DC_{,kk} - 2\frac{\kappa G^{\beta}}{\Omega\eta}\left(\hat{\varepsilon}_{ij,ij} + \frac{\nu^{\beta}}{1-2\nu^{\beta}}\hat{\varepsilon}_{kk,ii}\right) \tag{41}$$

with the effective diffusivity

$$D = \frac{2\kappa}{\eta}\left(\frac{1-\nu^{\alpha}}{1-2\nu^{\alpha}}G^{\alpha} + \frac{1-\nu^{\beta}}{1-2\nu^{\beta}}G^{\beta}\right) \tag{42}$$

Inhomogeneous deformation of concurrent viscoelasticity and poroelasticity can exhibit complex dynamics. In the limited space here we present a brief discussion by relating the theory to the discussion of time and length in §II, and to other theories as limiting cases. Examples in §IV show that, even for a rheological model of a single dashpot, viscoelasticity proceeds over multiple times, depending on types of deformation. All these times scale with $\tau_v = \hat{G}^\beta / G^\beta$. Similarly, poroelasticity is characterized by multiple effective diffusivities, which will scale with D defined by Eq.(42). We will still use τ_v and D to discuss scaling. The two parameters are specific to the material model, and define a material-specific length $\sqrt{D\tau_v}$, a length over which the solvent spreads during the time of τ_v.

First consider an observation made over a large length, $L >> \sqrt{D\tau_v}$. When the time of observation is comparable to the time of poroelastic relaxation, $t \sim L^2/D$, we observe poroelastic relaxation, with elastic constants being those after viscoelastic relaxation. Such poroelastic deformation has been analyzed for elastomeric gels[42–44]. When the time of observation is even longer than the time of poroelastic deformation, $t >> L^2/D$, both poroelastic and viscoelastic relaxation have completed, and the gel behaves as a compressible elastic solid, with a constant chemical potential set by that in the environment, $\mu = \bar{\mu}$. When the time of observation is comparable to the time of viscoelastic relaxation, $t \sim \tau_v$, poroelastic relaxation has yet started, and we observe viscoelastic deformation. The concentration of the solvent is unchanged, $C = C_0$, we set $\varepsilon_{kk} = \hat{\varepsilon}_{kk} = 0$, and the gel behaves as an incompressible viscoelastic material. When the time is even shorter than the time of viscoelastic relaxation, $t << \tau_v$, neither viscoelasticity nor poroelasticity has started, and the gel behaves as an incompressible elastic solid.

Next consider an observation made over a short length, $L << \sqrt{D\tau_v}$. When the time of observation is comparable to the time of poroelastic relaxation, $t \sim L^2/D$, we observe poroelastic relaxation, with elastic constants being those before viscoelastic relaxation. When the time of observation is even shorter than the time of poroelastic deformation, $t << L^2/D$, both poroelastic and viscoelastic relaxation have yet started, and the gel behaves as an incompressible elastic solid. When the time of observation is comparable to the time of viscoelastic relaxation, $t \sim \tau_v$, solvent has sufficient time to spread over the length of observation, and gel behaves as a compressible viscoelastic solid, with a constant chemical potential set by that in the environment, $\mu = \bar{\mu}$. When the time is even longer than the time of viscoelastic relaxation, $t >> \tau_v$, both viscoelasticity and poroelasticity have completed, and the gel behaves as a compressible elastic solid.

VI. FINITE DEFORMATION

To focus on main ideas, in the above we have restricted the theory to infinitesimal deformation. Elastomeric gels, however, typically undergo finite deformation. The finite deformation considerably complicates the free energy function and the kinetic model. The structure of the theory, however, remains unchanged. The two subsections below paraphrase §III and §V in terms of finite deformation.

6.1. Homogeneous States

Consider homogeneous states first (Fig.4). Since we are no longer restricted to infinitesimal deformation from a state of equilibrium, here we choose a reference consisting of a unit cube of a dry polymer network, and an environment which is a pure liquid solvent in equilibrium with its own vapor, where the chemical potential of the solvent is set to be zero[54]. In the reference state, the dry polymer and the environment are not in equilibrium: the solvent is motivated to migrate into the network. In a current state, the network absorbs C number of solvent molecules, and deforms into a parallelepiped. The thermodynamic state of the block is invariant with respect to any rigid-body translation; we fix the position of one vertex of the block to the origin of the coordinates. In the reference state, the three edges of the cube are unit vectors lying on the coordinates. In the current state, the three edges of the parallelepiped are vectors of components F_{i1}, F_{i2} and F_{i3}. The nine components F_{iK} together define the tensor of the deformation gradient $\boldsymbol{F}$. In general, we will not make the assumption like Eq.(2), but will regard C and $\boldsymbol{F}$ as independent variables. The thermodynamic state of the block is also invariant with respect to any rigid-body rotation. That is, the thermodynamic state depends on the size and shape of the parallelepiped, but not on its orientation in space. The size and shape of the parallelepiped are fully determined by the lengths of, and the angles between, the three edges of the parallelepiped—that is, by the six inner products of the three vectors, $F_{iK}F_{iL}$, which is known as the Green tensor.

Attention is focused on isothermal processes, in which temperature is fixed and is not listed as a variable. Let W be the Helmholtz free energy of the block in the current state relative to the Helmholtz free energy of its constitutes in the reference state (i.e., the dry network and C number of solvent molecules in the pure liquid solvent in equilibrium with its own vapor). Let s_{iK} be the force applied on the block in the current state, in direction i, on the face whose normal vector is in direction K when the block is in the reference state. Because the block in the reference state is a unit cube, by definition s_{iK} are the components of the nominal stress tensor. The applied forces can be represented by hanging weights. In the current state, associated with a small change in the deformation gradient, $\delta \boldsymbol{F}$, the potential energy of the hanging weights changes by $-s_{iK}\delta F_{iK}$. Let μ be the chemical potential of the solvent in the environment in the current state—that is, the increase of the Helmholtz free energy of the environment when the environment gains one solvent molecule. Associated with the transfer of δC number of solvent molecules from the environment to the gel, the free energy of the environment changes by $-\mu\delta C$.

The gel, the hanging weights, and the environment together form a composite thermodynamic system. The composite exchanges energy with the rest of the world by heat, but not by work. The composite does not exchange matter with the rest of the world. The Helmholtz free energy of the composite is the sum of the Helmholtz free energy of the gel, the potential energy of the weights, and the Helmholtz free energy of the environment. Thermodynamics requires that the Helmholtz free energy of the composite should not increase:

$$\delta W - s_{iK}\delta F_{iK} - \mu\delta C \le 0 \tag{43}$$

The equality in (43) holds when the composite undergoes reversible changes around a state of equilibrium, and the inequality in (43) holds when the composite undergoes irreversible changes out of equilibrium.

The variation means the value of a quantity at a time minus that at a slightly earlier time. As usual in thermodynamics, this inequality involves the direction of time, but not the duration of time.

We characterize dissipative processes of the local rearrangement by using a set of internal variables, $\xi^1, \xi^2, \cdots$. For example, the internal variables can represent the deformation of the dashpot in the rheological model in Fig.5. These internal variables, along with the deformation gradient and the concentration of solvent, specify the nonequilibrium state of the gel. As part of the specification of the rheological model, the Helmholtz free energy of the gel is taken to be a function of these independent variables:

$$W = W\left(\boldsymbol{F}, C, \xi^1, \xi^2, \cdots\right) \tag{44}$$

According to the differential calculus, associated with small changes in the independent variables, the free energy changes by

$$\delta W = \frac{\partial W}{\partial F_{iK}}\delta F_{iK} + \frac{\partial W}{\partial C}\delta C + \sum_m \frac{\partial W}{\partial \xi^m}\delta\xi^m \tag{45}$$

A combination of Eqs.(43) and (45) gives that

$$\left(\frac{\partial W}{\partial C} - \mu\right)\delta C + \left(\frac{\partial W}{\partial F_{iK}} - s_{iK}\right)\delta F_{iK} + \sum_m \frac{\partial W}{\partial \xi^m}\delta\xi^m \le 0 \tag{46}$$

This condition (46) holds for arbitrary and independent small changes in C, F_{iK}, $\xi^1, \xi^2, \cdots$. We assume that, when the internal variables are fixed, the composite is in equilibrium with respect to changes in C and F_{iK}, so that

$$\mu = \frac{\partial W\left(\boldsymbol{F}, C, \xi^1, \xi^2, \cdots\right)}{\partial C} \tag{47}$$

$$s_{iK} = \frac{\partial W\left(\boldsymbol{F}, C, \xi^1, \xi^2, \cdots\right)}{\partial F_{iK}} \tag{48}$$

Because the thermodynamic state of the block is invariant with respect to any rigid-body rotation, W depends on $\boldsymbol{F}$ through the Green tensor $F_{iK}F_{iL}$. Consequently, Eq.(48) implies that $s_{iK}F_{jK} = s_{jK}F_{iK}$, which is also the condition of the balance of moment acting on the parallelepiped.

We assume that the system is not necessarily in equilibrium with respect to changes in the internal variables. Consequently, Eq.(46) becomes

$$\sum_m \frac{\partial W\left(\boldsymbol{F}, C, \xi^1, \xi^2, \cdots\right)}{\partial \xi^m} \delta \xi^m \leq 0 \tag{49}$$

This inequality describes the viscoelasticity of the gel, and is usually modeled by the rheological models composed of spring and dashpot. For example, a linear kinetic model

$$\frac{\mathrm{d}\xi^m(t)}{\mathrm{d}t} = -\sum_n N^{mn} \frac{\partial W}{\partial \xi^n} \tag{50}$$

satisfies Eq.(49) if the matrix N^{mn} is symmetric and positive-definite. A large body of literature on viscoelasticity exists and has been discussed recently elsewhere[55–57].

The model of homogeneous states can be summarized as follows. The gel is modeled as a nonequilibrium thermodynamic system of seven external degrees of freedom, one characterized by a pair of work-conjugate variables (C, μ), and the other six characterized by the work-conjugate variables (F_{iK}, s_{iK}). Recall that the state of the gel depends on $\boldsymbol{F}$ only through the six inner products $F_{iK}F_{iL}$. To fully characterize a state of the gel, we further specify a set of internal variables, $\xi^1, \xi^2, \cdots$. The external variables and the internal variables co-evolve according to equations of state (47) and (48), as well as the kinetic equations (50).

6.2. Inhomogeneous States

Next consider the evolution of a gel through a sequence of inhomogeneous states. Once again, a gel is regarded as a sum of many small pieces, and each piece evolves in time through homogeneous states, following the theory developed in the previous subsection. Communication between the pieces is described by the kinematics of deformation, balance of forces, conservation of the solvent, and kinetics of the migration of the solvent. All these are identical to those in the poroelastic theory of gels[54].

The reference state is taken to be a dry network. Let an element of the body occupy a place of coordinate $\boldsymbol{X}$ when the body is in the reference state. In the current state at time t, the element $\boldsymbol{X}$ moves to a new place of coordinates $\boldsymbol{x}$. The function $\boldsymbol{x} = \boldsymbol{x}(\boldsymbol{X}, t)$ describes the field of deformation of the gel evolving in the time. The deformation gradient relates to the field of deformation as

$$F_{iK} = \frac{\partial x_i(\boldsymbol{X}, t)}{\partial X_K} \tag{51}$$

Let $B_i(\boldsymbol{X}, t)$ be the body force on an element in the current state divided by the volume of the element in the reference state. The balance of the forces requires that

$$\frac{\partial s_{iK}(\boldsymbol{X}, t)}{\partial X_K} + B_i = 0 \tag{52}$$

Let $T_i(\boldsymbol{X}, t)$ be the force on an element of surface in the current state divided by the area of the element in the reference state. The balance of forces requires that

$$s_{iK} N_K = T_i \tag{53}$$

where N_K is the unit vector normal to the element in the reference state.

Let C be the nominal concentration of the solvent, namely, the number of solvent molecules in an element in the current state divided by the volume of the element in the reference state. Let J_K be the nominal flux of the solvent, i.e., $J_K N_K$ is the number of solvent molecules per unit time flowing through an element of a surface divided by the area of the element in the reference state. The conservation of the number of solvent molecules requires that

$$\frac{\partial C(\boldsymbol{X}, t)}{\partial t} + \frac{\partial J_K(\boldsymbol{X}, t)}{\partial X_K} = 0 \tag{54}$$

Let i is the number of solvent molecules per unit time injected into the body through an element of the surface divided by the area of the element in the reference state. The conservation of the number of solvent molecules requires that

$$-J_K N_K = i \tag{55}$$

Let $\mu(\boldsymbol{X}, t)$ be the field of chemical potential of the solvent in the body. A commonly used kinetic model is that the flux is linear in the gradient of the chemical potential:

$$J_K = -M_{KL} \frac{\partial \mu(\mathbf{X}, t)}{\partial X_L} \tag{56}$$

where the mobility M_{KL} is taken to be a symmetric and positive-definite tensor.

The body is submerged in an environment in which the chemical potential of the solvent is $\bar{\mu}$. Thermodynamics dictates that the combined free energy of the gel, the mechanism that applies forces, and the environment should not increase:

$$\int \frac{\delta W}{\delta t} \mathrm{d}V - \int B_i \frac{\delta x_i}{\delta t} \mathrm{d}V - \int T_i \frac{\delta x_i}{\delta t} \mathrm{d}A - \int \bar{\mu} i \mathrm{d}A \le 0 \tag{57}$$

This inequality, using (45), (47), (48), (51)-(55) and the divergence theorem, reduces to

$$\int \left[\sum_m \frac{\partial W}{\partial \xi^m} \frac{\delta \xi^m}{\delta t} + J_K \frac{\partial \mu}{X_K} \right] \mathrm{d}V \le 0 \tag{58}$$

This thermodynamic inequality places a restriction on kinetic models. For example, the kinetic models (50) and (56) satisfy this inequality.

VII. CONCLUDING REMARKS

Elastomeric gels evolve by the conformational change of the polymer network and the migration of the solvent, resulting in the macroscopic behavior of concurrent viscoelasticity and poroelasticity. We describe an approach to differentiate viscoelasticity and poroelasticity by experimental observations over different times and different lengths. We develop a theory of concurrent viscoelasticity and poroelasticity. The theory is structured at two levels: the kinetics of viscoelasticity is described by using the homogeneous states of a material element, and kinetics of poroelasticity is described by using the inhomogeneous states in a body. Several examples illustrate viscoelasticity-limited solvent migration, where solvent migration is fast and the rate of change is limited by viscoelasticity. The theory of evolving inhomogeneous states is related to various theories in limiting cases. We have restricted the analysis to isothermal processes, where temperature is kept uniform in space and constant in time. Consequently, we do not list temperature as a variable, and uses the Helmholtz free energy to formulate the theory. If we wish to include the effects of inhomogeneous and time-dependent temperature field, we should invoke the second law in terms of entropy. It is hoped that these ideas will be used to analyze time-dependent phenomena in elastomeric gels, and to enable experimental characterization of elastomeric gels using familiar methods such as compression and indentation.

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