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A theory for species migration in a finitely strained solid with application to polymer network swelling[☆]

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ABSTRACT

We present a theory for the behavior of a solid undergoing two interdependent processes, a macroscopic or mechanical process due to the deformation of the solid and a microscopic or chemical process due to the migration of a chemical species through the solid. The principle of virtual power is invoked to deduce the basic balances of the theory, namely the mechanical force balance and the transport balance for the chemical species. In combination with thermodynamically consistent constitutive relations, these balances generate the basic equations of the theory. Keeping in mind applications involving the swelling of polymer networks by liquids, a specialization of the theory is presented and applied to study the influences of mechanical and chemical interactions on equilibrium states and diffusive dynamical processes. It is shown that the possibility of a mechanically induced phase transition is governed by two parameters: the Flory interaction parameter and a parameter given by the product between the number of cross-linked units per unit reference volume and the molecular volume of the liquid molecule. As for diffusion, it is shown that the theory is able to describe the pressure-induced diffusion in swollen membranes.

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1. Introduction

In his famous treatise on thermodynamics, Gibbs (1878) advanced a treatment for the equilibrium of elastic solids capable of absorbing fluids. Gibbs showed that the notion of chemical potential for a fluid absorbed in a solid is definable and may include the effect of the state of strain in the solid. Along with the recognition of the gradient of chemical potential as the driving force for diffusion, this breakthrough formed a basis for subsequent works on the interaction between mechanics and chemistry in solids capable of absorbing chemical species, a subject of great importance to many applications. Most notably, in metallurgy, Gibbs' approach led to the development of modern theories for solid solutions under stress (see Larché and Cahn, 1985 and the references cited therein).

Gibbs' approach is also relevant to polymer science, where a rich variety of challenging problems arise in connection with the swelling of polymer networks. These problems include phase transitions and pattern formation in gels (Onuki, 1993; Tanaka et al., 1987) and anomalous diffusion (Crank, 1990). In this context, Gibbs' approach was basic for the development of the classical theory of swelling equilibria (Flory, 1953; Treloar, 1975). However, contrary to the

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developments in metallurgy, most non-equilibrium theories do not follow Gibbs' idea of a multi-component solid but rely on alternative conceptual pictures. One exception is Neogi et al. (1986) who considered a small-strain theory of diffusion in polymers based on the theory for chemomechanical diffusion introduced by Larché and Cahn (1982). So many dynamical theories of swelling-related problems have been proposed that mentioning, let alone comparing, all different approaches is a formidable task that is beyond the scope of this work. Notwithstanding this, it is worth mentioning the works by Durning and Morman (1993), Barriere and Leibler (2003), and Doi (2009) on swelling dynamics, and Rajagopal (2003) for a review of diffusion. It is important to emphasize that the notion of multi-component body introduced by Gibbs corresponds to the notion of a solid with microstructure, as Fried and Gurtin (1999) note.

The purpose of this work is two-fold: (i) to develop a general finite-strain theory for the mutual interaction between mechanics and chemistry for solids capable of absorbing fluid-like chemical species, following Gibbs' idea of solid with microstructure; (ii) to investigate the influence of mechanics on the existence of multiphase equilibria in polymeric gels and on the diffusion of liquids through polymer networks.

The general theory is developed along the lines presented by Fried and Gurtin (1999) except for the treatment of the basic balance laws, that are here deduced by adopting the virtual-power format proposed by Podio-Guidugli (2009). Accordingly, in choosing the forms of the internal and external power expenditures, mechanical and chemical aspects are considered on the same footing. Specifically, the chemical potential is viewed as a generalized velocity conjugate to generalized chemical forces; mechanical and chemical external forces are split into their inertial and non-inertial parts. We also introduce a mechanical version of the second law of thermodynamics that involves the total energy and the applied external power associated with mechanical and chemical interactions. With appropriate prescriptions for the inertial forces, we arrive at final expressions for the basic laws identical to those used by Fried and Gurtin. These are standard force balance, a conservation equation for the fluid-like component, and a dissipation inequality. In particular, the conservation law for the fluid-like component follows from the chemical force balance.

Our approach to the constitutive theory begins by the multiplicative decomposition of the deformation gradient into its mechanical and chemical parts, in which the latter provides a link between the mechanical (macro) and chemical (micro) structures (Duda and Souza, 2002). After using the procedure of Coleman and Noll (1963), we show that the constitutive response is specified by functions determining the chemical strain, the free-energy density, and the fluid mobility. For a special mechanochemical environment, we introduce the canonical free-energy and show that its critical points correspond to equilibrium states. A particular specialization of the general theory, which employs the constitutive assumptions for the chemical strain and free-energy density adopted by Treloar (1975), is then presented. This theory, which for a special environment reduces to Treloar's equilibrium theory, is singled out for detailed study. Specifically, we illustrate the application of the theory through the analysis of the swelling equilibria of and the diffusion of liquids through polymer networks in one dimension. In particular, we obtain a necessary condition, which involves the constitutive parameters, for stress-induced phase coexistence, a condition which turns out to be also a necessary condition for uphill (or backward) diffusion. In addition, we show that the predictions of the theory are in very good agreement with an experimental result concerning the pressure-induced steady-state diffusion of a liquid through a polymeric membrane.

The finite-strain theories of fluid diffusion in elastic solids presented by Durning and Morman (1993), Baek and Srinivasa (2004), and Hong et al. (2008) share our view of a fluid–solid mixture as a single continuum body but adopt different approaches to deriving governing equations. Most importantly, these works are based on the assumption that the body is fully immersed in a fluid bath. This limits the range of applicable loading conditions. In particular, the theory of Durning and Morman (1993) is developed for bodies loaded exclusively by the pressure exerted by an encompassing fluid bath, while the theories of Baek and Srinivasa (2004) and Hong et al. (2008) treat the body comprised by the solid–fluid mixture and the surrounding fluid bath as a system and allow for an extra traction at the interface between the body and the bath. Here, the body is not required to be totally immersed in a fluid bath. This allows for the consideration of more general classes of mechanochemical environments. Boundary conditions aside, the bulk equations used by Durning and Morman (1993) and Hong et al. (2008) can also be obtained from the theory presented here.

The remainder of this paper is organized as follows. In Section 2, the general theoretical framework is developed. In Section 3, the general framework is specialized to the case of a polymer network that can absorb solvent molecules. In Section 4, the specialized theory is applied to study the equilibria and diffusive dynamical processes in a right-circular cylindrical specimen with lateral boundary constrained by a rigid impermeable sleeve, one end free, the other end fixed, and with different reservoir pressures at its ends. Finally, in Section 5, a summary of our key results is presented.

2. General theory

Consider a solid \mathcal{B} capable of absorbing a fluid-like chemical species, or simply a fluid for the sake of brevity, where \mathcal{B} is identified with a region of space that the solid occupies in a fixed reference configuration.

We view \mathcal{B} as a platform for interdependent processes taking place at two different scales, a macroscopic (mechanical) process due to the deformation of the solid and a microscopic (chemical) process due to the migration of the fluid through the solid. The kinematics of these processes are assumed to be described by the vector field \mathbf{y} representing the mechanical motion and by the scalar field α representing the *chemical motion*. The corresponding *realizable velocities* are denoted by $\mathbf{v} = \dot{\mathbf{y}}$ and $\mu = \dot{\alpha}$, with the latter being interpreted as the chemical potential. Notice that by their very definitions, these

velocities, as functions of points in \mathcal{B} , measure tendencies to change in the shape and composition of \mathcal{B} . For a similar interpretation of the chemical potential see [Baierlein \(2001\)](#) and [Job and Herrmann \(2006\)](#).

For later reference, we denote by c_s and ρ the solid content and mass per unit reference volume, respectively, and, granted that the solid component is conserved, observe that $\dot{c}_s = 0$ and $\dot{\rho} = 0$. In addition, we denote by c the fluid content per unit reference volume.

To deduce all relevant balance and imbalance laws, we follow an approach pioneered by [Podio-Guidugli \(2009\)](#) for multiphysics theories like ours and exemplified by him in a thermomechanical context, in which the counterparts of the quantities α and $\dot{\alpha}$ are the thermal displacement and temperature, respectively. It is worth mentioning that the analogy between chemical potential and the inverse of the temperature has been recognized by many authors and is suggested by certain basic developments of statistical mechanics.

2.1. Virtual powers

We assume that the dynamics of \mathcal{B} are specified in terms of a pair of linear, bounded, and continuous functionals, referred to as the internal and external power expenditures, defined for any part \mathcal{P} of \mathcal{B} and a given collection $\mathcal{V} = (\delta\mathbf{y}, \delta\alpha)$ of continuously differentiable virtual velocities. For any part $\mathcal{P} \subset \mathcal{B}$, the internal virtual power is defined by

$$\mathcal{W}_i(\mathcal{P}; \delta\mathbf{y}, \delta\alpha) := \int_{\mathcal{P}} (\mathbf{S} \cdot \nabla \delta\mathbf{y} + \mathbf{h} \cdot \nabla \delta\alpha) dv, \quad (1)$$

where \mathbf{S} and \mathbf{h} represent internal mechanical and chemical interactions of the first order. Further, for any part $\mathcal{P} \subset \mathcal{B}$, the external virtual power is defined by

$$\mathcal{W}_e(\mathcal{P}; \delta\mathbf{y}, \delta\alpha) := \int_{\partial\mathcal{P}} (\mathbf{s}_{\partial\mathcal{P}} \cdot \delta\mathbf{y} + h_{\partial\mathcal{P}} \delta\alpha) da + \int_{\mathcal{P}} (\mathbf{b}^e \cdot \delta\mathbf{y} + h^e \delta\alpha) dv, \quad (2)$$

where $\mathbf{s}_{\partial\mathcal{P}}$ and $h_{\partial\mathcal{P}}$ represent mechanical and chemical contact interactions and \mathbf{b}^e and h^e represent mechanical and chemical interactions at a distance.

More specifically, external fields \mathbf{b}^e and h^e account for interactions with all bodies external to \mathcal{B} . This leads to decompositions of \mathbf{b}^e and h^e into non-inertial, or applied, and inertial parts. The non-inertial parts of \mathbf{b}^e and h^e account for interactions of bodies accessible to observation, whereas the inertial parts of \mathbf{b}^e and h^e account for interactions with bodies in the remaining universe. See the discussion provided by [Truesdell \(1991\)](#).

For the present purposes, we adopt the following decompositions of \mathbf{b}^e and h^e :

$$\mathbf{b}^e = \mathbf{b} - \dot{\mathbf{p}} \quad \text{and} \quad h^e = h - \dot{c}, \quad (3)$$

where \mathbf{b} and h are the non-inertial parts of \mathbf{b}^e and h^e , $-\dot{\mathbf{p}}$ and $-\dot{c}$ are the inertial parts of \mathbf{b}^e and h^e , and \mathbf{p} is the *momentum* per unit reference volume. These choices for the mechanical and chemical forces of inertia can be understood as follows. First, recall that \mathcal{B} , which is viewed as the seat of two interdependent processes, can undergo changes in two important attributes: its quantity of motion or momentum and its composition. Classically, the mechanical force of inertia is associated with momentum changes. In the same way, we stipulate that the chemical force of inertia is associated with composition changes, which here are exclusively associated with changes in the fluid content.

On substituting (3) into (2), it follows that the external power \mathcal{W}_e admits the decomposition

$$\mathcal{W}_e = \mathcal{W}_e^{\text{ni}} + \mathcal{W}_e^{\text{in}} \quad (4)$$

into a “non-inertial” part $\mathcal{W}_e^{\text{ni}}$ and an “inertial” part $\mathcal{W}_e^{\text{in}}$, with

$$\mathcal{W}_e^{\text{ni}}(\mathcal{P}; \delta\mathbf{y}, \delta\alpha) := \int_{\mathcal{P}} (\mathbf{b} \cdot \delta\mathbf{y} + h \delta\alpha) dv + \int_{\partial\mathcal{P}} (\mathbf{s}_{\partial\mathcal{P}} \cdot \delta\mathbf{y} + h_{\partial\mathcal{P}} \delta\alpha) da \quad (5)$$

and

$$\mathcal{W}_e^{\text{in}}(\mathcal{P}; \delta\mathbf{y}, \delta\alpha) := - \int_{\mathcal{P}} (\dot{\mathbf{p}} \cdot \delta\mathbf{y} + \dot{c} \delta\alpha) dv. \quad (6)$$

The *principle of virtual power*, which is assumed to hold at each fixed time, states that, for any part \mathcal{P} of \mathcal{B} ,

$$\mathcal{W}_i(\mathcal{P}; \delta\mathbf{y}, \delta\alpha) = \mathcal{W}_e(\mathcal{P}; \delta\mathbf{y}, \delta\alpha) \quad (7)$$

for each pair $(\delta\mathbf{y}, \delta\alpha)$ in \mathcal{V} . This principle implies the mechanical and chemical balances

$$\text{Div} \mathbf{S} + \mathbf{b} = \dot{\mathbf{p}} \quad \text{and} \quad \text{Div} \mathbf{h} + h = \dot{c} \quad \text{on } \mathcal{P}, \quad (8)$$

together with the traction conditions

$$\mathbf{S} \mathbf{n} = \mathbf{s}_{\partial\mathcal{P}} \quad \text{and} \quad \mathbf{h} \cdot \mathbf{n} = h_{\partial\mathcal{P}} \quad \text{on } \partial\mathcal{P}, \quad (9)$$

where \mathbf{n} is the exterior unit normal to $\partial\mathcal{P}$.

Finally, notice that (8)₁ is the local form of the balance equation for the momentum, with \mathbf{S} and \mathbf{b} representing the momentum flux and supply, respectively. Likewise, (8)₂ is the local form of the balance equation for the fluid content, with \mathbf{h} and h representing the fluid flux and supply, respectively. The standard form of the balance equation for the fluid content

is obtained upon the identification $\mathbf{h} = -\mathbf{j}$, an identification we shall use from now on without further remark. We refer to \mathbf{j} as the referential flux of the fluid relative to the solid.

2.2. Dissipation inequality

Following [Fried and Gurtin \(1994\)](#), we now consider a mechanical version of the second law of thermodynamics by introducing an inequality called henceforth the dissipation inequality. This inequality, which involves the additional notion of energy, states that the energy of an arbitrary part \mathcal{P} of \mathcal{B} cannot increase at a rate faster than the power expended on \mathcal{P} by the applied forces. This statement can be written as

$$\frac{d}{dt} \int_{\mathcal{P}} e \, dv \leq \mathcal{W}_e^{\text{mi}}(\mathcal{P}; \mathbf{v}, \mu), \quad (10)$$

where e is the energy density per unit reference volume. Notice that this inequality is essentially the same as presented by [Fried and Gurtin \(1994\)](#) except for the fact that their energy was split into its free and kinetic parts and that only mechanical inertia was considered. It is also interesting to note that (10) resembles the isothermal version of the extension of the Truesdell work inequality presented by [Man \(1989\)](#).

On using (4), (5), and (7), it follows from (10) that

$$\dot{e} - \mu \dot{c} - \dot{\mathbf{p}} \cdot \mathbf{v} - \mathbf{S} \cdot \dot{\mathbf{F}} + \mathbf{j} \cdot \nabla \mu \leq 0. \quad (11)$$

After assuming the classical expression $\mathbf{p} = \rho \mathbf{v}$ for the momentum density, introducing the standard notion of specific kinetic energy $\kappa = \rho |\mathbf{v}|^2 / 2$, and recalling that $\dot{\rho} = 0$, it follows from (11) that

$$\dot{\psi} - \mu \dot{c} - \mathbf{S} \cdot \dot{\mathbf{F}} + \mathbf{j} \cdot \nabla \mu \leq 0, \quad (12)$$

where $\psi := e - \kappa$ is defined as the free-energy density. This inequality is the same presented in (2.24) of [Fried and Gurtin \(1999\)](#).

2.3. Constitutive theory and governing equations

We consider shape changes undergone by \mathcal{B} as the result of two deformation processes, a mechanical process due to stress and a chemical process induced by transport of the fluid-like component. To account for these processes, we adopt a multiplicative decomposition

$$\mathbf{F} = \mathbf{F}_m \mathbf{F}_d \quad (13)$$

of the deformation gradient \mathbf{F} into mechanical and chemical parts \mathbf{F}_m and \mathbf{F}_d , with

$$J_d = \det \mathbf{F}_d > 0. \quad (14)$$

Neither \mathbf{F}_m nor \mathbf{F}_d is required to be a gradient and \mathbf{F}_d can be viewed as a mapping taking vectors in the reference configuration into vectors in a local intermediate configuration. It is interesting to note that a special version of (13) was adopted by [Flory and Rehner \(1944\)](#) to rectify an incorrect conclusion they had drawn in their seminal work ([Flory and Rehner, 1943](#)) on the swelling of polymer networks. This original use of the multiplicative decomposition, however, seems to have been overlooked by subsequent works, including the recent paper by [Lubarda \(2004\)](#), which presents a detailed survey of the multiplicative decomposition and its applications in thermoelasticity, elastoplasticity, and biomechanics.

Keeping in mind applications related to the swelling of polymer networks, we also assume the mechanical deformation is isochoric, so that volume changes are solely due to the fluid-induced deformation:

$$\det \mathbf{F}_m = 1, \quad \det \mathbf{F} = \det \mathbf{F}_d. \quad (15)$$

We also assume that the fluid-induced strain is defined by the constraint

$$\mathbf{F}_d = \hat{\mathbf{F}}_d(c), \quad (16)$$

which implies that

$$\mathbf{L}_d := \dot{\mathbf{F}}_d \mathbf{F}_d^{-1} = \dot{c} \mathbf{G} \quad \text{and} \quad \mathbf{G} = \frac{d\hat{\mathbf{F}}_d(c)}{dc} \hat{\mathbf{F}}_d^{-1}(c). \quad (17)$$

Notice that \mathbf{G} embodies the tensorial character of the fluid-induced strain and that in the isotropic case \mathbf{G} is spherical.

After taking (13) and (17) into account, it follows that the stress power is given by

$$\mathbf{S} \cdot \dot{\mathbf{F}} = \mathbf{P} \cdot \dot{\mathbf{F}}_m + (\mathbf{F}_m^T \mathbf{P} \cdot \mathbf{G}) \dot{c}, \quad (18)$$

where

$$\mathbf{P} = \mathbf{S} \mathbf{F}_d^T. \quad (19)$$

Since the stress tensor \mathbf{P} is power-conjugate to the time rate $\dot{\mathbf{F}}_m$, we might view $J_d^{-1} \mathbf{P}$ as the Piola stress with respect to the intermediate configuration. Moreover, the tensor $J_d^{-1} \mathbf{F}_m^T \mathbf{P}$ is the Mandel stress and the quantity

$$\boldsymbol{\tau} := \mathbf{F}_m^T \mathbf{P} \cdot \mathbf{G} \tag{20}$$

in (18) may be viewed as a resolved stress.

In view of the constraint (15)₁, we assume that

$$\mathbf{P} = \mathbf{P}_R + \mathbf{P}_A, \tag{21}$$

where \mathbf{P}_R and \mathbf{P}_A are the reactive and active parts of \mathbf{P} , respectively, and

$$\mathbf{P}_R \cdot \dot{\mathbf{F}}_m = 0 \tag{22}$$

for all $\dot{\mathbf{F}}_m$ compatible with (15)₁. Therefore, using standard arguments, it follows that

$$\mathbf{P}_R = -q \mathbf{F}_m^{-T}, \tag{23}$$

where q is an arbitrary, in the sense of being constitutively indeterminate, field. Using (21) and (20), we arrive at

$$\boldsymbol{\tau} = (\mathbf{F}_m^T \mathbf{P}_A - q \mathbf{I}) \cdot \mathbf{G}. \tag{24}$$

In view of (18), (23), and (24), the free-energy imbalance (12) can be rewritten as

$$-\dot{\psi} + \mathbf{P}_A \cdot \dot{\mathbf{F}}_m + (\mu + \tau) \dot{c} - \mathbf{j} \cdot \nabla \mu \geq 0. \tag{25}$$

Guided by the inequality (25), we consider constitutive equations

$$\psi = \hat{\psi}(\mathbf{F}_m, c, \nabla \mu), \quad \mathbf{P}_A = \hat{\mathbf{P}}(\mathbf{F}_m, c, \nabla \mu), \quad \mu + \tau = \hat{\gamma}(\mathbf{F}_m, c, \nabla \mu), \quad \mathbf{j} = \hat{\mathbf{j}}(\mathbf{F}_m, c, \nabla \mu), \tag{26}$$

giving ψ , \mathbf{P}_A , $\mu + \tau$, and \mathbf{j} as functions of \mathbf{F}_m , c , and $\nabla \mu$.

Following Coleman and Noll (1963), we require that the constitutive response be such that the inequality (25) holds identically for all choices of $(\dot{\mathbf{F}}_m, \dot{c}, \nabla \dot{\mu})$ and $(\mathbf{F}_m, c, \nabla \mu)$. We thereby conclude that:

1. The constitutive function $\hat{\psi}$ must be independent of $\nabla \mu$, i.e.,

$$\hat{\psi}(\mathbf{F}_m, c, \nabla \mu) = \hat{\psi}(\mathbf{F}_m, c). \tag{27}$$

2. The equilibrium relations

$$\hat{\mathbf{P}}(\mathbf{F}_m, c, \nabla \mu) = \frac{\partial \hat{\psi}(\mathbf{F}_m, c)}{\partial \mathbf{F}_m} \quad \text{and} \quad \hat{\gamma}(\mathbf{F}_m, c, \nabla \mu) = \frac{\partial \hat{\psi}(\mathbf{F}_m, c)}{\partial c} \tag{28}$$

must hold.

3. The internal dissipation inequality

$$\hat{\mathbf{j}}(\mathbf{F}_m, c, \nabla \mu) \cdot \nabla \mu \leq 0 \tag{29}$$

must hold for all choices of $(\mathbf{F}_m, c, \nabla \mu)$.

Granted sufficient smoothness, it can be shown that (29) implies the representation

$$\hat{\mathbf{j}}(\mathbf{F}_m, c, \nabla \mu) = -\mathbf{M}(\mathbf{F}_m, c, \nabla \mu) \nabla \mu, \tag{30}$$

where \mathbf{M} is a positive semidefinite tensor-valued function related to the fluid mobility.

From now on, we suppose that \mathbf{M} is a positive-definite tensor function whenever c does not vanish. This is tantamount to stipulating that $\nabla \mu = \mathbf{0}$ if and only if no dissipation occurs. Therefore, the constitutive theory is characterized by the constitutive functions $\hat{\psi}$ and \mathbf{M} , with the former being independent of $\nabla \mu$ and the latter being a positive-definite tensor function for $c \neq 0$.

Keeping in mind (16), it is convenient to define the response function $\tilde{\psi}(\mathbf{F}, c) := \hat{\psi}(\mathbf{F} \mathbf{F}_d^{-1}, c)$. With this definition, it follows that

$$\frac{\partial \tilde{\psi}(\mathbf{F}, c)}{\partial \mathbf{F}} = \frac{\partial \hat{\psi}(\mathbf{F}_m, c)}{\partial \mathbf{F}_m} \mathbf{F}_d^{-T} \tag{31}$$

and that

$$\frac{\partial \tilde{\psi}(\mathbf{F}, c)}{\partial c} = \frac{\partial \hat{\psi}(\mathbf{F}_m, c)}{\partial c} - \mathbf{F}_m^T \frac{\partial \hat{\psi}(\mathbf{F}_m, c)}{\partial \mathbf{F}_m} \cdot \mathbf{G}, \tag{32}$$

where \mathbf{G} is given by (17)₂. Further, using (19), (21), (23), and (28) it follows that the Piola stress tensor \mathbf{S} and the chemical potential μ can be written as

$$\mathbf{S} = \frac{\partial \tilde{\psi}(\mathbf{F}, c)}{\partial \mathbf{F}} - q \mathbf{F}^{-\top} \quad \text{and} \quad \mu = \frac{\partial \tilde{\psi}(\mathbf{F}, c)}{\partial c} + q \operatorname{tr} \mathbf{G}. \quad (33)$$

It is also convenient to define the response function $\hat{\mathbf{M}}$ by the expression $\hat{\mathbf{M}}(\mathbf{F}, c, \nabla \mu) := \mathbf{M}(\mathbf{F} \mathbf{F}_d^{-1}, c, \nabla \mu)$. With this, the fluid flow \mathbf{j} can be written as

$$\mathbf{j} = -\hat{\mathbf{M}}(\mathbf{F}, c, \nabla \mu) \nabla \mu, \quad (34)$$

where μ is given by (77)₂.

The governing equations are obtained through the combination of the aforementioned basic balances (see (8)) and constitutive relations (see (13), (15), (16), (33), and (34)). The corresponding field equations can be written as

$$\left. \begin{aligned} \det \mathbf{F} &= \det \hat{\mathbf{F}}_d(c), \\ \operatorname{Div} \left(\frac{\partial \tilde{\psi}(\mathbf{F}, c)}{\partial \mathbf{F}} - q \mathbf{F}^{-\top} \right) + \mathbf{b} &= \rho \dot{\mathbf{v}}, \\ \dot{c} &= \operatorname{Div}(\hat{\mathbf{M}}(\mathbf{F}, c, \nabla \mu) \nabla \mu) + h, \end{aligned} \right\} \quad (35)$$

where $\mathbf{F} = \nabla \mathbf{y}$.

The treatment of boundary conditions is standard. Boundary conditions for (35)₂ involve the prescription of either \mathbf{y} or $\mathbf{S} \mathbf{n}$, whereas boundary conditions for (35)₃ involve the prescription of either α or $\mathbf{j} \cdot \mathbf{n} = -\hat{\mathbf{M}}(\mathbf{F}, c, \nabla \mu) \mu \cdot \mathbf{n}$.

2.4. Mechanochemical environment

We suppose that B is immersed in a chemical environment wherein the chemical potential of the fluid-like component is constant and equal to μ_a . We also suppose that the fluid-component supply-rate h vanishes. One portion of ∂B , say $\partial_l B$, is impermeable, whereas chemical equilibrium with the environment prevails on the complementary portion, say $\partial_E B$, of the boundary. Therefore, the following boundary conditions hold:

$$\mu(\mathbf{X}, t) = \mu_a, \quad \mathbf{X} \in \partial_E B, \quad \mathbf{j}(\mathbf{X}, t) \cdot \mathbf{n}(\mathbf{X}) = 0, \quad \mathbf{X} \in \partial_l B, \quad (36)$$

Notice that (36)₁ is equivalent to the prescription $\alpha(\mathbf{X}, t) = \mu_a t$. For later reference, we mention that for the case in which the environment is constituted by a pure and incompressible liquid solution, the chemical potential μ_a is given by

$$\mu_a = \mu^0 + p_a v, \quad (37)$$

where μ^0 is a reference chemical potential, p_a is the hydrostatic pressure of the liquid, and v the molecular volume of a liquid molecule.

As for the mechanical environment, we suppose that

$$\mathbf{y}(\mathbf{X}, t) = \mathbf{d}(\mathbf{X}), \quad \mathbf{X} \in \partial_d B, \quad \mathbf{S}(\mathbf{X}, t) \mathbf{n}(\mathbf{X}) = \mathbf{s}(\mathbf{X}, t), \quad \mathbf{X} \in \partial_s B, \quad (38)$$

where the prescribed “displacement” \mathbf{d} and the prescribed traction \mathbf{s} are given functions on $\partial_d B$ and $\partial_s B$, which are two disjoint complementary sets of ∂B , respectively. We also require that the loading environment be conservative, i.e., we require that there exists a potential energy $\mathcal{L}[\mathbf{y}]$, which for every motion \mathbf{y} compatible with (38)₁ satisfies

$$\dot{\mathcal{L}}[\mathbf{y}] = - \int_B \mathbf{b} \cdot \dot{\mathbf{y}} \, dv - \int_{\partial_s B} \mathbf{s} \cdot \dot{\mathbf{y}} \, da. \quad (39)$$

One important class of loading environments of the type described above is defined by the following expression for \mathcal{L} :

$$\mathcal{L}[\mathbf{y}] = \int_B \tilde{\varphi}(\mathbf{F}) \, dv, \quad \tilde{\varphi}(\mathbf{F}) = -\boldsymbol{\Sigma} \cdot \mathbf{F} + \boldsymbol{\Lambda} \cdot \mathbf{F}^* + \varpi \det \mathbf{F}, \quad (40)$$

where $\boldsymbol{\Sigma}$, $\boldsymbol{\Lambda}$, and ϖ are constants, and where

$$\mathbf{F}^* = (\det \mathbf{F}) \mathbf{F}^{-\top} \quad (41)$$

is the adjugate of \mathbf{F} . Important examples include the dead-load environment for which $\boldsymbol{\Lambda} = \mathbf{0}$ and $\varpi = 0$, and the spatially dependent pressure loading for which $\boldsymbol{\Lambda} = \mathbf{0}$ and $\boldsymbol{\Sigma} = \mathbf{0}$.

Now let us suppose that $\partial_E B$ is non-empty and define the canonical free-energy functional \mathcal{F} by the expression

$$\mathcal{F}[\mathbf{y}, c] = \int_B (\tilde{\psi}(\mathbf{F}, c) - \mu_a c) \, dv + \mathcal{L}[\mathbf{y}]. \quad (42)$$

It is worth noticing that \mathcal{F} enters the Liapunov relation

$$\overline{\left(\mathcal{F}[\mathbf{y}, c] + \int_B \frac{1}{2} \rho |\mathbf{v}|^2 \, dv \right)} \leq 0, \quad (43)$$

a relation which is easily obtained using (10). Moreover, the critical points of \mathcal{F} correspond to equilibrium solutions of (35) for the specific environment under consideration, as will be discussed below.

We turn our attention now to equilibrium solutions of (35) compatible with the environment described previously. These solutions are time-independent and do not involve dissipation. The latter observation implies, after bearing in mind that \mathbf{M} is positive-definite, along with (29) and (30), that \mathbf{j} vanishes. Therefore, (36)₂ is trivially satisfied and the chemical potential is constant and, from (36)₁, equal to μ_a . On using (33)₂, we arrive at

$$\mu = \frac{\partial \tilde{\psi}(\mathbf{F}, c)}{\partial c} + q \operatorname{tr} \mathbf{G} = \mu_a. \tag{44}$$

Therefore, it is easy to see that an equilibrium solution can be obtained by solving (35)₁, (35)₂ with a null right-hand side, and (44). Notice that (35)₃ is trivially satisfied.

We now delineate a procedure to show that the problem of finding equilibrium solutions is equivalent to the problem of determining the critical points of \mathcal{F} subject to the constraint (35)₁ or, equivalently, to determining the critical points of the functional $\hat{\mathcal{F}}$ defined by

$$\hat{\mathcal{F}}[\mathbf{y}, c, q] = \mathcal{F}[\mathbf{y}, c] - \int_{\mathcal{B}} q \left(\frac{\det \mathbf{F}}{\det \mathbf{F}_d} - 1 \right) dv, \tag{45}$$

where q is a Lagrange multiplier. In fact, the critical points of $\hat{\mathcal{F}}$ satisfy

$$\delta \hat{\mathcal{F}}[\mathbf{y}, c, q](\delta \mathbf{y}, \delta c, \delta q) = 0 \tag{46}$$

for every variation $\delta \mathbf{y}$, δc , and δq , where given a functional \mathcal{G} of $[\mathbf{y}, c, q]$,

$$\delta \mathcal{G}[\mathbf{y}, c, q](\delta \mathbf{y}, \delta c, \delta q) := \frac{d}{d\varepsilon} \mathcal{G}[\mathbf{y} + \varepsilon \delta \mathbf{y}, c + \varepsilon \delta c, q + \varepsilon \delta q]_{\varepsilon=0} \tag{47}$$

defines its first variation. Observe that

$$\delta \mathcal{F}[\mathbf{y}, c](\delta \mathbf{y}, \delta c) = \int_{\mathcal{B}} \left(\frac{\partial \tilde{\psi}(\mathbf{F}, c)}{\partial \mathbf{F}} \cdot \nabla \delta \mathbf{y} + \left(\frac{\partial \tilde{\psi}(\mathbf{F}, c)}{\partial c} - \mu_a \right) \delta c \right) dv + \delta \mathcal{L}[\mathbf{y}](\delta \mathbf{y}), \tag{48}$$

with

$$\delta \mathcal{L}[\mathbf{y}](\delta \mathbf{y}) = - \int_{\mathcal{B}} \mathbf{b} \cdot \delta \mathbf{y} dv - \int_{\partial \mathcal{B}} \mathbf{s} \cdot \delta \mathbf{y} da, \tag{49}$$

and that the first variation of the second term of the right hand side of (45) is given by

$$- \int_{\mathcal{B}} (q \mathbf{F}^* \cdot \nabla \delta \mathbf{y} + q \det \mathbf{F} \operatorname{tr} \mathbf{G} \delta c + \delta q (\det \mathbf{F} - \det \mathbf{F}_d)) \frac{dv}{\det \mathbf{F}_d}. \tag{50}$$

Finally, the conclusion that the critical points of $\hat{\mathcal{F}}$ are equilibrium solutions of (35) follows by using (46), (48)–(50), along with integration by parts, the divergence theorem, and the fundamental lemma of the calculus of variations.

The following remark is in order. For the situations in which (35)₁ can be inverted to write c as a function of $\det \mathbf{F}$, the canonical free-energy functional can be rewritten solely in terms of \mathbf{y} . Consequently, the problem of finding equilibrium solutions can be viewed as a nonlinear elasticity problem.

3. Specialization

We now present a special theory in which the solid \mathcal{B} is a polymer network that can absorb solvent molecules. In this setting, it is convenient to identify \mathcal{B} with a fixed reference configuration free of solvent molecules (i.e., with a dry polymer network). In this case, the solid content c_s per unit reference volume represents the number of cross-linked units per unit reference volume.

The specialization is based on classical constitutive choices for $\hat{\mathbf{F}}_d$, $\hat{\psi}$, and $\hat{\mathbf{M}}$, as discussed below. Following the approach of Flory (1953) and Treloar (1975), we assume that the fluid-induced strain is volumetric and that both the polymer and the solvent are “incompressible.” These assumptions together result in the following expression for $\hat{\mathbf{F}}_d$

$$\hat{\mathbf{F}}_d(c) = (\det \mathbf{F}_d)^{1/3} \mathbf{I}, \quad \det \mathbf{F}_d = 1 + v c, \tag{51}$$

where v is the volume of one solvent molecule. It therefore follows from (15) and (17)₂ that

$$\det \mathbf{F} = 1 + v c \quad \text{and} \quad \mathbf{G} = \frac{1}{3} v (1 + v c)^{-1} \mathbf{I}. \tag{52}$$

The free-energy density $\tilde{\psi}$ takes into account three contributions: the energy of the “unmixed” pure solvent; the elastic energy due to network deformation; and the energy of mixing. Invoking the Frenkel–Flory–Rehner hypothesis—discussed, for example, by Flory (1953)—we assume that the latter two contributions are additive and separable. It then follows that

$$\tilde{\psi}(\mathbf{F}, c) = \mu^0 c + \tilde{\psi}_e(\mathbf{F}) + \tilde{\psi}_m(c), \tag{53}$$

where μ^0 is the chemical potential of the pure solvent, and where the elastic and mixing contributions are given by

$$\tilde{\psi}_e(\mathbf{F}) = \frac{1}{2}c_S k_B T (|\mathbf{F}|^2 - 3) \quad (54)$$

and

$$\tilde{\psi}_m(c) = k_B T c (\ln(1-\phi) + \chi\phi). \quad (55)$$

Here and throughout this paper, k_B is Boltzmann's constant, T is the absolute temperature, χ is the Flory–Huggins interaction parameter, and

$$\phi = \frac{1}{1 + \nu c} \quad (56)$$

is the polymer volume fraction. The elastic contribution corresponds to Gaussian network theory (e.g., Treloar, 1975), whereas the mixing contribution is given by the Flory–Huggins expression (e.g., Flory, 1953). The parameter χ , which characterizes the interaction between polymer and solvent molecules, is positive for attraction and negative for repulsion.

We explore now some consequences of the preceding constitutive assumptions. First, we conclude from (33), (41), (52), and (56), that the Piola stress \mathbf{S} and the chemical potential μ are given by

$$\mathbf{S} = c_S k_B T \mathbf{F} - q\phi \mathbf{F}^* \quad (57)$$

and

$$\mu = \mu^0 + k_B T (\ln(1-\phi) + \phi + \chi\phi^2) + \nu q\phi. \quad (58)$$

These equations, together with the expression $\mathbf{S} = \mathbf{T}\mathbf{F}^*$ relating the Piola stress \mathbf{S} to the Cauchy stress \mathbf{T} , imply that

$$\mathbf{T} = (c_S k_B T \phi \mathbf{F}\mathbf{F}^T - \pi \mathbf{I}) - p \mathbf{I}, \quad (59)$$

with

$$p := \frac{\mu - \mu^0}{\nu} \quad \text{and} \quad \pi := -\frac{k_B T}{\nu} (\ln(1-\phi) + \phi + \chi\phi^2). \quad (60)$$

Recall that for a permeable body in equilibrium with its surroundings, the chemical potential is constant and equal to the ambient chemical potential, which is given by (37) for an environment composed of a pure liquid solution. In this case, it is easy to see that p is equal to the ambient pressure p_a . For this reason, we interpret p as the *fluid pressure*. Notice also that the first term on the right-hand side of (59) vanishes whenever $\phi = 0$. For this reason we refer to $c_S k_B T \phi \mathbf{F}\mathbf{F}^T - \pi \mathbf{I}$ as the *network stress*. Therefore, \mathbf{T} may be viewed as the sum of a network stress and a fluid stress. Furthermore, the network stress has two contributions, one elastic and one due to mixing.

It is worth relating p to the notion of osmotic pressure. To achieve this, we begin by observing that (59) implies that the hydrostatic stress $\sigma_h := -\text{tr}\mathbf{T}/3$ is given by

$$\sigma_h = -\frac{1}{3}c_S k_B T \phi |\mathbf{F}|^2 + \pi + p. \quad (61)$$

This implies that (58) can be written as

$$\mu = \hat{\mu}(\sigma_h, \mathbf{F}, \phi) := \mu^0 + \nu(\sigma_h - \pi + \frac{1}{3}c_S k_B T \phi |\mathbf{F}|^2). \quad (62)$$

Following Flory (1953) (see also Onuki, 1993), we define the osmotic pressure Π by the relation

$$\nu \Pi = \hat{\mu}(\sigma_h, \mathbf{F}, 0) - \hat{\mu}(\sigma_h, \mathbf{F}, \phi), \quad (63)$$

which, by using (62), implies that

$$\Pi = \pi - \frac{1}{3}c_S k_B T \phi |\mathbf{F}|^2, \quad (64)$$

with the first and second terms representing, respectively, the mixing and elastic contributions to the osmotic pressure. Notice that upon substituting (64) into (62), it follows that

$$p = \sigma_h - \Pi, \quad (65)$$

which shows that the fluid pressure p is the difference between the total hydrostatic pressure and the osmotic pressure.

As for the mobility $\hat{\mathbf{M}}$, we content ourselves with the following constitutive assumption:

$$\hat{\mathbf{M}}(\mathbf{F}, c, \nabla\mu) = \hat{m}(c)(\mathbf{F}^{-1}\mathbf{F}^*)^T, \quad (66)$$

where \hat{m} is positive-valued function for $c \neq 0$. In this case, it follows from (30) that

$$\mathbf{j} = -\hat{m}(c)(\mathbf{F}^{-1}\mathbf{F}^*)^T \nabla\mu, \quad (67)$$

where μ is given by (58). Observe that this choice for the mobility tensor corresponds to the standard relation

$$\mathbf{j} = -\hat{m}(c) \text{grad } \mu \quad (68)$$

between the spatial flux \mathbf{j} and spatial chemical potential gradient $\text{grad } \mu$, as can be easily seen after substituting $\mathbf{j} = \mathbf{F}^{*T} \mathbf{j}$ and $\nabla\mu = \mathbf{F}^T \text{grad } \mu$ into (67).

In view of the relation (56), notice that the composition can be represented either by c or by ϕ . In particular, the governing equations in (35) can be viewed as field equations for either (\mathbf{y}, q, c) or (\mathbf{y}, q, ϕ) . In fact, after stipulating that $\mathbf{b} = \mathbf{0}$ and $h=0$ and taking into account the aforementioned constitutive assumptions, the governing equations in (35) reduce to the equations

$$\left. \begin{aligned} \phi \det \mathbf{F} &= 1, \\ \nabla(q\phi) &= c_s k_B T \phi \mathbf{F}^\top \text{Div } \mathbf{F}, \\ \dot{\phi} &= v \phi^2 \text{Div } \mathbf{j}, \end{aligned} \right\} \quad (69)$$

for \mathbf{y} , q , and ϕ , with \mathbf{j} and μ given by (67) and (58), respectively. It is worth emphasizing that (52)₂ can be used to write c in terms of $\det \mathbf{F}$.

Moreover, the specialized theory is defined in terms of the parameters c_s , v , and χ , and the constitutive function m . Notice also that the parameter c_s is often written as $c_s = \rho/M_c$, where M_c is the weight per chain (Flory, 1953; Treloar, 1975).

In the next section we illustrate the applicability of the theory developed so far by investigating the following one-dimensional problems: the equilibrium of a swollen bar under tension and the pressure-induced diffusion of a liquid through a polymeric membrane. General aspects that are common to both examples are discussed first.

4. Application

Consider a cylindrical body \mathcal{B} identified with a cylindrical region

$$\mathcal{B} := \{(X, R, \Theta) | 0 \leq X \leq L, 0 \leq R \leq A, 0 \leq \Theta < 2\pi\}, \quad (70)$$

with length L and radius A . A point $\mathbf{X} = (X, R, \Theta)$ in \mathcal{B} is mapped by the motion \mathbf{y} into a point (x, r, θ) in $\mathbf{y}(\mathcal{B}, t)$. Suppose that, after being fitted into a rigid tube of radius a , \mathcal{B} has one of its ends ($X = 0$) attached to a rigid porous substrate, while the other end ($X = L$) remains free. The cylinder is then placed in contact with two pure liquid solutions, one at pressure p_0 on the surface $X = 0$ and the other at pressure p_L on the surface $X = L$. Chemical equilibrium is presumed to prevail on these surfaces. Additionally, the surface $X = L$ is subject to a normal traction σ and the lateral surface $R=A$ of the body is presumed to be impermeable and in permanent and frictionless contact with the tube wall. Keeping in mind (37), we express these stipulations via boundary conditions:

- On the surface $X=0$:

$$x = X, \quad r = \eta R, \quad \theta = \Theta, \quad \mu = \mu^0 + p_0 v. \quad (71)$$

- On the surface $X=L$:

$$\mathbf{S} \mathbf{e}_X = (-\eta^2 p_L + \sigma) \mathbf{e}_X, \quad \mu = \mu^0 + p_L v. \quad (72)$$

- On the lateral surface $R=A$:

$$r = a, \quad \mathbf{S} \mathbf{e}_R \cdot \mathbf{t} = 0, \quad \mathbf{j} \cdot \mathbf{e}_R = 0. \quad (73)$$

Here and throughout the following, $\eta = a/A$ is the radial reduction, \mathbf{e}_X is the unit vector along the axis of the cylinder, \mathbf{e}_R is the unit vector along the radial direction, and \mathbf{t} is an arbitrary vector tangent to the lateral surface of the cylinder. Observe that (71) asserts that the insertion of the cylinder into the tube causes a uniform deformation of the cross-section $X = 0$. The presence of η in (72)₁ accounts for the fact that although p_L is defined in the spatial configuration, a referential description is being used. The condition involving \mathbf{t} represents the assumption that the interface between the cylinder and the tube is frictionless.

Our aim is to solve (69) under the conditions described above. We will consider both equilibria and diffusive dynamical processes.

We assume that the motion \mathbf{y} is given by

$$x = f(X, t), \quad r = \eta R, \quad \theta = \Theta, \quad (74)$$

where the function f obeys $f(0, t) = 0$. Notice that this choice for \mathbf{y} satisfies the mechanical boundary conditions (71)_{1,2,3} and (73)₁.

The deformation gradient \mathbf{F} associated with (74) has the matrix representation

$$[\mathbf{F}] = \text{diag}\{\lambda, \eta, \eta\}, \quad (75)$$

where $\lambda(X, t) := \partial f(X, t) / \partial X$. This implies that

$$\det \mathbf{F} = \eta^2 \lambda \quad \text{and} \quad \text{Div } \mathbf{F} = \frac{\partial \lambda}{\partial X} \mathbf{e}_X, \quad (76)$$

and, using (58), that the stress tensor \mathbf{S} has the matrix representation

$$[\mathbf{S}] = \text{diag} \left\{ c_S k_B T \lambda - \frac{q}{\lambda}, c_S k_B T \eta - \frac{q}{\eta}, c_S k_B T \eta - \frac{q}{\eta} \right\}. \quad (77)$$

Notice that the boundary condition (73)₂ is trivially satisfied.

We now explore the consequences that the Ansatz (74) imposes on the fields ϕ and q satisfying (69). First, notice that by using (69)₁ and (76)₁ it follows that

$$\phi \lambda \eta^2 = 1, \quad (78)$$

which implies that $\phi(\mathbf{X}, t) = \phi(X, t)$. Keeping this in mind, it follows from (69)₂ that $q(\mathbf{X}, t) = q(X, t)$ and, by using (78) to express λ in terms of ϕ , that

$$\frac{\partial(q(X, t)\phi(X, t))}{\partial X} = \frac{\partial}{\partial X} \left(\frac{c_S k_B T}{\eta^4 \phi(X, t)} \right). \quad (79)$$

If we integrate (79) with respect to X , we find that

$$q\phi = \frac{c_S k_B T}{\eta^4 \phi} + K, \quad (80)$$

where K is obtained by appealing to the mechanical boundary condition (72)₁, which now can be written as

$$c_S k_B T \lambda(L, t) - \frac{q(L, t)}{\lambda(L, t)} = -\eta^2 p_L(t) + \sigma(t). \quad (81)$$

Together with (78) and (80), (81) yields

$$K = p_L - \frac{\sigma}{\eta^2}. \quad (82)$$

Therefore, by (80) and (82),

$$q\phi = \frac{c_S k_B T}{\eta^4 \phi} + p_L - \frac{\sigma}{\eta^2}. \quad (83)$$

This expression allows us to obtain q once ϕ is known.

We now consider the problem of determining ϕ . First, notice that (58) and (83) imply that the chemical potential can be viewed as a function of ϕ , say $\mu = \hat{\mu}(\phi)$. This fact, (67) and (75) imply that $\mathbf{j} = \mathbf{j}_e \mathbf{x}$ —which implies that the chemical boundary condition on the lateral surface of the cylinder is satisfied identically—with \mathbf{j} given by

$$\mathbf{j} = -\frac{\partial g(\phi)}{\partial X}, \quad (84)$$

where g is defined by the relation

$$g'(\phi) = \eta^4 \phi m(\phi) \hat{\mu}'(\phi). \quad (85)$$

In (85) and henceforth, a superposed prime stands for the derivative with respect to ϕ and, keeping (56) in mind, $m(\phi) := \hat{m}(c)$. In particular, (69)₃ reduces to

$$\dot{\phi} = v \phi^2 \frac{\partial^2 g(\phi)}{\partial X^2}. \quad (86)$$

To determine ϕ , we must solve (86), which requires two boundary conditions. These conditions follow from the chemical boundary conditions at $X=0$ and $X=L$. In fact, on using (58), (71)₃, and (83), we conclude that

$$\frac{1}{\phi_0} + \eta^4 \gamma (\ln(1 - \phi_0) + \phi_0 + \chi \phi_0^2) = \frac{\eta^2}{c_S k_B T} ((p_0 - p_L) \eta^2 + \sigma), \quad (87)$$

where $\phi_0(t) := \phi(0, t)$ and

$$\gamma = \frac{1}{c_S v}. \quad (88)$$

In a similar fashion, it follows that

$$\frac{1}{\phi_L} + \eta^4 \gamma (\ln(1 - \phi_L) + \phi_L + \chi \phi_L^2) = \frac{\eta^2 \sigma}{c_S k_B T}, \quad (89)$$

where $\phi_L(t) := \phi(L, t)$. To find ϕ we must therefore solve (86) with the boundary conditions $\phi(0, t) = \phi_0(t)$ and $\phi(L, t) = \phi_L(t)$, with ϕ_0 and ϕ_L being solutions of (87) and (89), respectively.

Therefore, if (74) is assumed, (69) reduces to a one-dimensional problem involving the unknowns f , q , and ϕ . Notice that, with the knowledge of ϕ , f can be obtained by integrating $1/(\eta^2 \phi)$ and using the boundary condition $f(0, t) = 0$.

It is interesting to note that, after defining the diffusion coefficient by the relation $j = -D\partial c/\partial X$, it follows from (56) and (84) that

$$D = -v\eta^4\phi^3 m(\phi)\hat{\mu}'(\phi). \tag{90}$$

This expression shows that the sign of the diffusion coefficient is defined by the sign of $\hat{\mu}'$. A simple calculation shows that for a good solvent, i.e., for $\chi \leq \frac{1}{2}$, $\hat{\mu}'(\phi) \leq 0$ for all $\phi \in (0, 1)$, which implies that the coefficient diffusion is non-negative. Otherwise, $\hat{\mu}$ may be not monotonic, which indicates the possibility of a negative diffusion coefficient. For a negative diffusion coefficient, solvent molecules move from low to high concentration regions, a phenomenon known as uphill (or backward) diffusion. It is interesting to note that the (lack of) monotonicity of $\hat{\mu}$ gives rise to the (lack of) monotonicity of the stress-strain curve that will be discussed next.

For the sake of simplicity, we assume from now on that $\eta = 1$.

4.1. Equilibria

Suppose that $\phi = \phi_e$, with ϕ_e constant, satisfies simultaneously the boundary conditions (87) and (89). In this case, it follows immediately that (86) is satisfied and that $p_0 = p_L = p_a$ is a necessary condition for the existence of such solution. The boundary conditions also give the equation to be solved for ϕ_e . This equation can be expressed as

$$\bar{\sigma} = \hat{\sigma}(\phi_e), \tag{91}$$

where $\bar{\sigma}$ and $\hat{\sigma}$ are given by

$$\bar{\sigma} := \frac{\sigma}{c_S k_B T}, \quad \hat{\sigma}(\phi) := \frac{1}{\phi} + \gamma(\ln(1-\phi) + \phi + \chi\phi^2). \tag{92}$$

Notice that the environment under consideration is of the general type considered previously. In particular, the potential energy is given by (40), in which $\Sigma = \text{diag}\{\sigma, 0, 0\}$, $\Lambda = \mathbf{0}$, and $\varpi = p_a$. Therefore, it can be shown that for ϕ constant, the corresponding canonical free-energy, normalized by $\pi A^2 L c_S k_B T$ and modulo an inconsequential additive constant, can be written as

$$\bar{\mathcal{F}}_\sigma(\phi) = \frac{1}{2} \left(\frac{1}{\phi^2} - 2 \right) + \gamma \frac{1-\phi}{\phi} (\ln(1-\phi) + \chi\phi) - \frac{\sigma}{\phi c_S k_B T}. \tag{93}$$

A direct calculation then shows that

$$\bar{\mathcal{F}}'_\sigma(\phi) = \frac{\bar{\sigma} - \hat{\sigma}(\phi)}{\phi^2} \quad \text{and} \quad \bar{\mathcal{F}}''_\sigma(\phi) = -\frac{\hat{\sigma}'(\phi)}{\phi^2} - 2\frac{\bar{\sigma} - \hat{\sigma}(\phi)}{\phi^3}. \tag{94}$$

As discussed earlier, (93) and (94) show that equilibrium solutions are critical points of \mathcal{F} , which are stable (local minima of \mathcal{F}) whenever the quantity $\hat{\sigma}$ defined in (92)₂ obeys $\hat{\sigma}' \leq 0$.

We begin by investigating the issue of existence of solutions of (91). We observe that $\hat{\sigma}$ is continuous on (0,1), that

$$\lim_{\phi \rightarrow 0} \hat{\sigma}(\phi) = +\infty \quad \text{and that} \quad \lim_{\phi \rightarrow 1} \hat{\sigma}(\phi) = -\infty.$$

Therefore, $\hat{\sigma}$ maps (0,1) onto the real line which implies that (91) admits a solution ϕ_e for a given $\bar{\sigma}$. As discussed before, such a solution is stable if $\hat{\sigma}'(\phi_e) \leq 0$ and unstable otherwise. The possibility of multiple solutions, a prerequisite for phase coexistence, is indicated by the condition $\hat{\sigma}' < 0$ over a portion of (0,1). Hence, the behavior of $\hat{\sigma}$ is crucial for the analysis of both stability and uniqueness of solutions.

Keeping (78) in mind, the problem under consideration is equivalent to the problem of equilibrium of a bar in a soft device examined by Ericksen (1975). In that work, Ericksen showed that a non-monotonic stress-strain relation could be used to describe certain aspects of stress-induced phase transitions in solids. Ericksen's analysis was seminal to subsequent works on the modeling of solid-solid phase transitions within the framework of continuum mechanics. The entire analysis performed by Ericksen could be applied here. However, our main goal is to establish a condition involving the constitutive parameters that brings about a non-monotonic stress-strain relation, whereby a necessary condition for stress-induced phase coexistence is established. It is noteworthy that a non-monotonic stress-strain relation is equivalent to the non-monotonicity of $\hat{\mu}$ since $\hat{\sigma}' = \hat{\mu}'$. Therefore, the analysis that ensues may also be relevant for the analysis of uphill diffusion.

To investigate the influence of the parameters χ and γ on the behavior of $\hat{\sigma}'$, we begin by introducing

$$\hat{\chi}(\phi, \gamma) := \frac{1}{2(1-\phi)} + \frac{1}{2\gamma\phi^3}, \tag{95}$$

and observing that a simple calculation using the definition of $\hat{\sigma}$ shows that $\hat{\sigma}'(\phi)$ and $\chi - \hat{\chi}(\phi, \gamma)$ have the same sign. Moreover, for each γ , $\hat{\chi}$ has the property that its minimum is attained at ϕ_c , i.e., $\chi_c(\gamma) := \hat{\chi}(\phi_c, \gamma) \leq \hat{\chi}(\phi, \gamma)$, where ϕ_c is

given by

$$\phi_c = \frac{-\varepsilon + \sqrt{\varepsilon^2 + 4\varepsilon}}{2}, \quad \varepsilon = \frac{3}{\sqrt{\gamma}}. \tag{96}$$

Notice that ϕ_c belongs to $(0,1)$, goes to 0 as ε goes to 0, and goes to 1 as ε goes to ∞ . Notice also that $\chi_c(\gamma)$ decreases as γ increases and goes to $\frac{1}{2}$ as γ goes to ∞ . As a result of the previous observations, it follows that if $\chi \leq \chi_c(\gamma)$, then $\hat{\sigma}'(\phi) \leq 0$ for all ϕ in $(0, 1)$, which implies that $\hat{\sigma}$ is monotonic. Otherwise, if $\chi > \chi_c(\gamma)$, then, by continuity, $\hat{\sigma}'(\phi) \leq 0$ and $\hat{\sigma}'(\phi) > 0$ over two non-empty and complementary portions of $(0,1)$, which implies that $\hat{\sigma}$ is not monotonic.

Additional insight can be gained through the analysis of the behavior of $\hat{\sigma}'$ in the (ϕ, χ) -plane. Fig. 1 depicts the (ϕ, χ) -diagram for different values of γ . This figure shows that for each γ there are two complementary regions in which $\hat{\sigma}' < 0$ (stable regimes) and $\hat{\sigma}' > 0$ (unstable regimes) separated by the set of points for which $\hat{\sigma}' = 0$. As noted before, observe that for each γ there is a special value of the mixing parameter χ below of which $\hat{\sigma}' < 0$. Furthermore, this values decreases as γ increases.

From the foregoing, it follows that a necessary and sufficient condition for a non-monotonic stress–strain relation is given by

$$\chi > \chi_c(\gamma). \tag{97}$$

This inequality provides a minimum requirement that the parameters χ and γ must obey for phase coexistence to occur. Recall that c_s and ν are properties of the polymer network and solvent, respectively. Thus, $\chi_c(\gamma)$ takes into account the polymer network and the solvent individually. The parameter χ , in contrast, accounts for the temperature-dependent interaction between the polymer network and the solvent. Usually, the interaction parameter decreases as the temperature increases. Fig. 2 shows that the (γ, χ) -plane is divided into two regions separated by the line representing the set of points for which $\chi = \chi_c(\gamma)$. If a pair (γ, χ) belongs to the upper region $\chi > \chi_c(\gamma)$, then phase coexistence is possible.

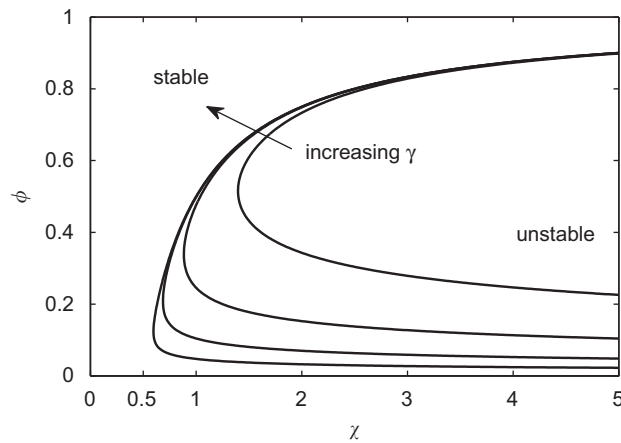


Fig. 1. (ϕ, χ) -diagram for different values of γ . The solid lines separate unstable and stable regions for the corresponding value of γ .

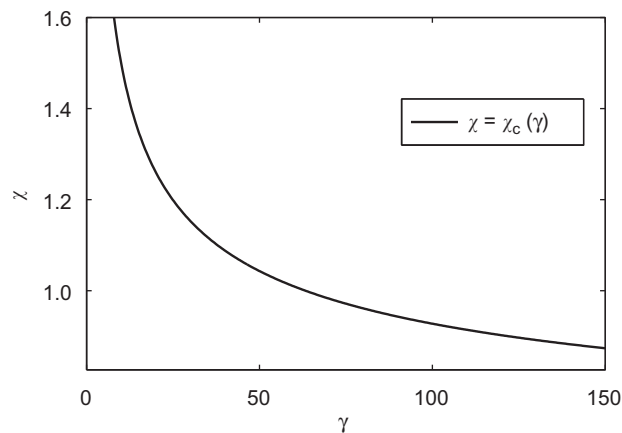


Fig. 2. (γ, χ) -diagram in which the solid line represents the set of points for which $\chi = \chi_c(\gamma)$. Phase transition is impossible for points below the solid line.

Otherwise, phase coexistence is impossible. Keeping in mind that $\gamma = 1/(c_s v)$, notice that, for χ and v fixed, there exists a value of c_s above which phase transition is impossible. Put another way, a sufficiently large value of the cross-link density c_s suppresses phase coexistence.

Dusek and Patterson (1968) were the first to predict phase coexistence in a polymeric-gel bars under uniaxial loading. In the problem studied by them, the bar is allowed to swell only transverse to the axial direction. Experimental results related to this configuration can be found in the works of Suzuki (1993) and Suzuki and Ishii (1999). In the present work, however, swelling is allowed only along the axial direction. This special situation has been discussed in many important works on phase transition in gels, including those of Onuki (1988), Sekimoto and Doi (1991), Tomari and Doi (1994), and Doi (2009). As the latter author remarks, the physical realization of the situation considered here presents the difficulty of ensuring the necessary lubrication between the specimen and the surrounding tube wall. In addition to that, we remark that it is also necessary to ensure that the lateral stress, which, by (77) and (83), is given by

$$c_s k_B T - \frac{1}{\phi} \left(\frac{c_s k_B T}{\phi} + p_a - \sigma \right) \tag{98}$$

is compressive. This implies that there is a maximum admissible value for σ .

4.2. Diffusion

Suppose now that $\sigma = 0$ and $\Delta p = p_L - p_0 > 0$. This situation corresponds to the problem of diffusion induced by the pressure difference Δp . Of particular interest here is the relation between the scalar flux j and the pressure difference Δp in the permanent regime.

We have that in the permanent regime the flux j is constant. Therefore, integration of (84) yields

$$jX = g(\phi_0) - g(\phi(X)), \tag{99}$$

where $\phi(0) = \phi_0$. On using the relation $\phi(L) = \phi_L$, this implies that

$$jL = g(\phi_0) - g(\phi_L). \tag{100}$$

The expression above provides a relation for j in terms of ϕ_0 and ϕ_L , which in their turn are calculated by using the boundary conditions (87) and (89). With this value of j , the corresponding ϕ is obtained simply by solving (99).

We now compare the prediction of (100) with the experimental result provided by Paul and Ebra-Lima (1970) for a rubber-toluene system in the permanent regime. To achieve this, it is necessary to identify the list of parameters (L, T, c_s, v, χ) as well as the function \hat{m} . The list of parameters was obtained from Paul and Ebra-Lima (1970). In addition, we assumed that \hat{m} is given by $\hat{m}(c) = Mc^n$, with $M > 0$ and $n \geq 1$ constants. See Table 1 for a complete list of all parameter values. The values of M and n were chosen with a view to understand their influences on the behavior of the system.

Fig. 3 depicts the relation between the volumetric flux, which is equal to $-vj$, and the pressure difference measured in pounds per square inch (psi). It is difficult to overlook the excellent agreement between the results. Fig. 4 shows the polymer fraction distribution for several values of Δp . Notice that the maximum and minimum values for the stretch are attained at $X=0$ and $X=L$, respectively.

The problem discussed above was also analyzed by Rajagopal and collaborators (e.g., Rajagopal, 2003) using a mixture-theoretic approach as well as for Baek and Srinivasa (2004) who used an alternative to Rajagopal's approach. In both cases, the results were also in very good agreement with experiments.

As for the transient regime, we content ourselves to show the evolution of polymer volume fraction profile for different instants until the steady state is reached. It is assumed that the surfaces of the initially dry membrane reach equilibrium instantaneously with the solution so that the boundary conditions given by (87) and (89) are adopted. The results obtained are depicted in Fig. 5.

It is noteworthy that the lateral stress, which in this case reduces to

$$c_s k_B T - \frac{c_s k_B T}{\phi^2} - p_L \tag{101}$$

is compressive and the maximum compression is attained at $X=L$. This kind of stress can lead to surface buckling instabilities (Tanaka et al., 1987).

Table 1
Parameters used in diffusion problem.

| | |
|---------------------|--|
| L | 0.0265 cm |
| c_s | 1.06×10^{-4} mol/cc |
| v | 106 cc/mol |
| χ | 0.425 |
| T | 30 °C |
| n | 3 |
| $M/(k_B T v^{n-1})$ | 3.46×10^{-5} cm ² /s |

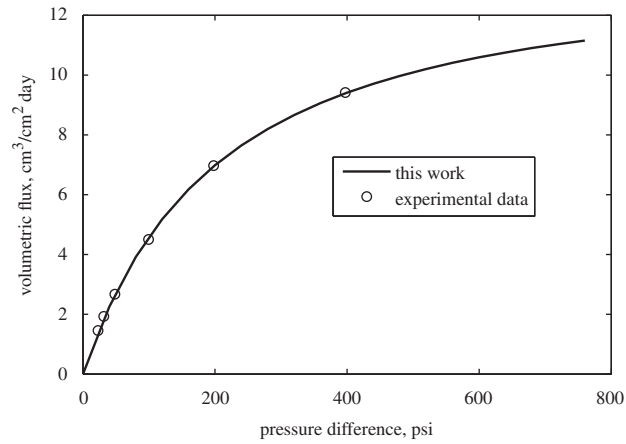


Fig. 3. Volumetric flux versus pressure difference: comparison with experimental results of Paul and Ebra-Lima (1970).

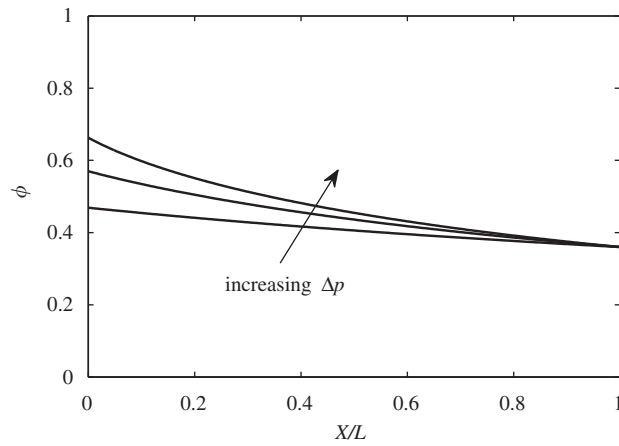


Fig. 4. Steady-state polymer volume fraction distribution for different values of the pressure difference.

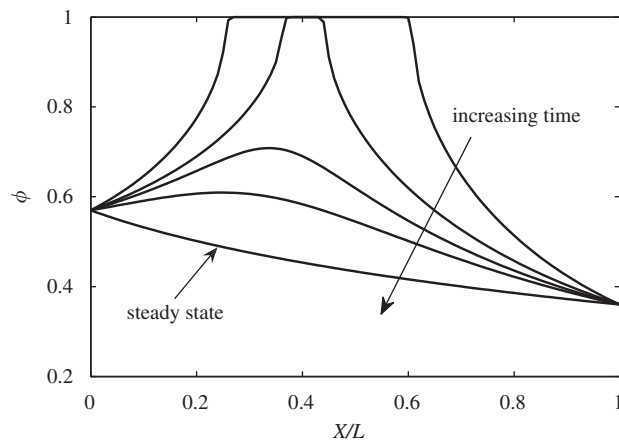


Fig. 5. Polymer volume fraction distribution at different instants for $\Delta p = 400$ psi.

5. Summary

In this work we presented a theory for the behavior of a solid undergoing two interdependent processes, a macroscopic or mechanical process due to the deformation of the solid and a microscopic or chemical process due to migration of a

chemical species through the solid. Our approach relied on the interpretation of the chemical potential for the migrating species as a generalized velocity associated with an extra kinematical descriptor. The principle of virtual power was then employed to generate the two basic balances of the theory: the mechanical force balance and the chemical force balance. The latter balance was used to deduce the transport balance for the chemical species. The governing equations were obtained after combining the basic balances with thermodynamically consistent constitutive relations, constitutive relations which hinged on the multiplicative decomposition of the deformation gradient into its mechanical and chemical parts. Keeping in mind applications in the context of swelling of polymer networks by liquids, a specialization of the theory was presented and applied to the study of the mutual interaction between mechanics and chemistry on equilibrium states and diffusive dynamical processes in the context of a one-dimensional problem. In particular, we showed that the possibility of a mechanically induced phase transition is governed by two parameters: the Flory interaction parameter and a parameter given by the product between the number of cross-linked units per unit reference volume and the molecular volume of the solvent. As for diffusion, we showed that the theory is able to describe the pressure-induced diffusion in swollen membranes.

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