# Contents

# 1 Introduction.

Mechanical theories describing polymer gels, and, more generally, a strained solid through which diffusion of a fluid takes place, have been put together using two different approaches. The early papers [4, 12] and the more recent work [5] model the gel as the superposition of two interacting continuous bodies: an incompressible solid, representing the polymeric network, and an incompressible fluid. The equations governing the evolution of these continua are obtained through an adaptation of Truesdell's theory of interacting continua [13]. Another series of papers [1, 11, 6, 7], adapt the original ideas of Gibbs [8] and Biot [2, 3] to model a polymeric gel as a single continuum whereby diffusion of a chemical species takes place, driven by the gradient of its chemical potential. Within this theory, constituive equations are obtained from a dissipation principle that takes explicitly into account the energetic flux associated to the motion of the fluid relative to the solid.

Given this state of matters provides a motivation to investigatate the relationships between the the two approaches. The contribution we give in this paper is twofold: we offer a revised exposition of the ideas in [4] in the special case when when the intercting continua are incompressible; we then show that the isothermal version of dissipation principle underlying the theory of gels within the setting of the *à la Biot* approach can be recovered, by making the appropriate identifications, from the corresponding principle in the setting of the theory of interacting continua.

# 2 Compound continua

## 2.1 Kinematics

**Index convention.** In the foregoing developments, the free index $\alpha$ runs between 1 and the number $N$ of constituents, while the free index $\beta$ runs between 2 and $N$:

$$\alpha \in \{1, \dots, N\}, \qquad \beta \in \{2, \dots, N\}.$$

The same convention is used for summations. Thus,

$$\sum_\alpha \equiv \sum_{\alpha=1}^N, \qquad \text{and} \qquad \sum_\beta \equiv \sum_{\beta=2}^N.$$

The subscript 1 shall be replaced by $s$ (standing for "solid") and, when there is only one fluid component, the subscript 2 shall be replaced by $f$ (standing for "fluid"). Accordingly:

- if $N = 2$ then $s \equiv 1$ and $f \equiv 2$.

### 2.1.1 The description of the motion of a compound continuum.

Generically speaking a *compound continuum* is a collection of $N$ continuum bodies, which we refer to as *constituents*, which can permeate each other by occupying the same region of space at the same time. The motion of each body is described in the same fashion as in standard continuum mechanics: one introduces a reference configurations $\mathcal{B}_\alpha$, where $\alpha = 1, \ldots, N$ is the index that labels the constituent; then the motion of the $\alpha$–th constituent of the mixture is specified by a function

$$\mathbf{x} = \boldsymbol{\chi}_\alpha(\boldsymbol{X}, t)$$

which associates to each material particle $\mathbf{X}$ in $\mathcal{B}_\alpha$ the position $\mathbf{x}$ occupied by that particle at time $t$. The functions $\boldsymbol{\chi}_\alpha(\mathbf{X}, t)$ are assumed to be smooth. In particular, the deformation gradients

$$\operatorname{Grad} \boldsymbol{\chi}_\alpha := \frac{\partial \boldsymbol{\chi}_\alpha}{\partial \mathbf{X}}, \qquad \text{eq:21} \tag{1}$$

and the velocities

$$\dot{\boldsymbol{\chi}}_\alpha := \frac{\partial \boldsymbol{\chi}_\alpha}{\partial t}, \qquad \text{eq:22} \tag{2}$$

are well defined. For $t$ fixed, the function $\boldsymbol{\chi}_\alpha(\cdot, t)$ is referred to as the *configuration* of the $\alpha$–th constituent at time $t$.

### 2.1.2 Eulerian and Lagrangean descriptions of a field.

Definitions (17) and (2) express the deformation gradient and the velocity as functions of the referential label $\mathbf{X}$. We say that these definitions provide a Lagrangean representation of these fields.

Now, mixture theory inherits from continuum mechanics the requirement that each configuration be a one-to-one mapping, thus forbidding interpenetration between parts of the same body. Because of this fact, given a Lagrangean field we can provide a Eulerian representation where the independent variable $\mathbf{X}$ is replaced by $\mathbf{x}$. For example, we define the spatial (Eulerian) velocity field of constituent $\alpha$ as:[1]

$$\mathbf{v}_\alpha(\mathbf{x}, t) = \dot{\boldsymbol{\chi}}_\alpha(\boldsymbol{\chi}_\alpha^{-1}(\mathbf{x}, t), t).$$

Of course, the reciprocal operation starting from a spatial field $\varphi(\boldsymbol{x}, t)$ can be carried out to define its Lagrangean (referential) representation

$$\Phi(\mathbf{X}, t) = \varphi(\boldsymbol{\chi}(\mathbf{X}, t), t).$$

In particular, given a spatial field $\varphi_\alpha(\mathbf{x}, t)$ related to component $\alpha$, the *material time derivative* of $\varphi$ *following the motion of the constituent* $\alpha$ is denoted by a grave accent:

$$\grave{\varphi}_\alpha := \frac{\partial \Phi_\alpha}{\partial t} = \frac{\partial \varphi_\alpha}{\partial t} + \operatorname{grad} \varphi_\alpha \cdot \mathbf{v}_\alpha. \qquad \text{eq:15} \tag{3}$$

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[1] Here $\boldsymbol{\chi}^{-1}(\cdot, t)$ denotes the inverse of the configuration $\chi_\alpha(\cdot, t)$ at time $t$.

When computing the time derivative of field that has already a subscript $\alpha$, we shall omit the double specification of the index $\alpha$ on top of the dot. If the field refers to a component $\beta$ different from $\alpha$, or to no component at all (in which case $\beta$ is to be omitted) we write

$$\overset{\alpha}{\dot{\varphi}}_{\beta} := \frac{\partial \Phi_{\beta}}{\partial t} = \frac{\partial \varphi_{\beta}}{\partial t} + \operatorname{grad} \varphi_{\beta} \cdot \mathbf{v}_{\alpha}. \qquad \text{eq:23} \tag{4}$$

**Convention.** Although $\varphi$ and $\Phi$ are different functions, they represent the same physical quantity. To avoid the proliferation of symbols, we shall avoid when possible using different symbols for the Lagrangean and Eulerian descriptions of a field. What description is being understood at a particular point of our development should be clear from the context.

## 2.2 Partial stresses and internal forces

A difference between mixture theory and conventional continuum theories is that different constituents can engage the same region of space. In fact, the images of two configurations $\boldsymbol{\chi}_{\alpha}(\cdot, t)$ and $\boldsymbol{\chi}_{\beta}(\cdot, t)$ $(\alpha \neq \beta)$ need not be disjoint. In other words, two distinct bodies may interpenetrate each other and interact. The token used in mixture theory to model the interactions between superposed constituent is an internal body force field that accompanies contact forces and the external body forces.The equilibrium equation that affirm balance between stress of a constituent, the external and the internal forces acting on a constituent may be derived through the principle of virtual powers. Additional properties shall be derived by recourse to invariance principles.

### 2.2.1 Internal and external powers.

Given a spatial region $\Omega$, the internal mechanical power expended within $\Omega$ is a linear functional of the individual velocities of the mixture costituents:

$$\mathscr{W}_{\text{int}}(\Omega)[\mathbf{v}_1, \ldots, \mathbf{v}_n] := \sum_{\alpha} \int_{\Omega} \left( \mathbf{T}_{\alpha} \cdot \operatorname{grad} \mathbf{v}_{\alpha} + \mathbf{f}_{\alpha} \cdot \mathbf{v}_{\alpha} \right). \tag{5}$$

The external power expended on the part occupying the spatial region $\Omega$ is

$$\mathscr{W}_{\text{ext}}(\Omega)[\mathbf{v}_1, \ldots, \mathbf{v}_n] := \sum_{\alpha} \left( \int_{\partial\Omega} \mathbf{t}_{\alpha} \cdot \mathbf{v}_{\alpha} + \int_{\Omega} \mathbf{b}_{\alpha} \cdot \mathbf{v}_{\alpha} \right). \tag{6}$$

### 2.2.2 Principle of virtual powers and balance equations.

The principle of virtual powers for every region $\Omega$ yields the pointwise form of the equilibrium equations

$$-\operatorname{div}\mathbf{T}_\alpha+\mathbf{f}_\alpha=\mathbf{b}_\alpha, \qquad \text{eq:35} \qquad (7)$$

as well as the *Cauchy's representation*:

$$\mathbf{t}_\alpha(\mathbf{x},\mathbf{n})=\mathbf{T}_\alpha(\mathbf{x})\mathbf{n} \qquad \text{eq:52} \qquad (8)$$

of the contact force $\mathbf{t}_\alpha$ acting at point $\mathbf{x}$ on the boundary of a region $\Omega$ whose outward unit normal is $\mathbf{n}$.

### 2.2.3 Invariance of the internal power.

The invariance of the internal power over superposed rigid velocities yields that the internal forces add up to null:

$$\sum_\alpha \mathbf{f}_\alpha=\mathbf{0},$$

and that the *total stress*:

$$\mathbf{T}:=\sum_\alpha \mathbf{T}_\alpha \in \mathrm{Sym}\,.$$

is a symmetric tensor:

$$\mathbf{T}\in \mathrm{Sym}\,.$$

The fields $\mathbf{T}_\alpha$ are called *partial stresses*. Although the need not be symmetric, their sum must be symmetric.

## 2.3 Further bits of kinematics

### 2.3.1 The bulk specific volume.

Since we leave inertial effects out of the picture, we shall not introduce the concept of mass and mass density. Instead, we shall make use of the notion of bulk specific volumes

$$\phi_\alpha=\frac{1}{\det\mathbf{F}_\alpha},$$

which obey the same laws of conservation as for mass in continuum mechanics:

lem:222 **Lemma 1.** *The bulk specific volumes obey:*

$$\grave{\phi}_\alpha + \phi_\alpha \operatorname{div} \mathbf{v}_\alpha = 0, \tag{9a}$$

*and, equivalently,*

$$\frac{\partial \phi_\alpha}{\partial t} + \operatorname{div}(\phi_\alpha \mathbf{v}_\alpha) = 0. \qquad \text{eq:11} \tag{9b}$$

The interpretation of the bulk specific volume is the following: consider a part $\mathcal{P}_\alpha$ of the body $\mathcal{B}_\alpha$. At a given time $t_0$, the material particles within the part $\mathcal{P}_\alpha$ will engage the spatial region

$$\Omega_\alpha = \boldsymbol{\chi}_\alpha(\mathcal{P}_\alpha, t_0).$$

If the diameter of $\mathcal{P}_\alpha$ is small compared to the characteristic scale of oscillation of the fields of interest (typically, this scale may be identified with the norm $|\mathbf{F}_\alpha|$ of the deformation gradient), then the volume of the spatial region $\Omega_\alpha$ is approximately:[2]

$$\operatorname{vol} \Omega_\alpha \simeq \phi_\alpha \operatorname{vol} \mathcal{P}_\alpha.$$

Thus, $\phi_\alpha$ accounts for how much of spatial volume is engaged by a unit volume in the reference configuration.

### 2.3.2 The true specific volume.

When referring to the region $\Omega_\alpha$ as being "engaged" by the part $\mathcal{P}_\alpha$ we purportedly do not use the verbal adjective "occupied". In fact, there is a class of physical systems, called *multicomponent mixtures*, that can be modeled by the theory of interacting continua (for example, a mixture of tiny air bubbles in water), but whose constituents are not truly superposed. For these systems, an observation performed

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[2] Let consider any extensive physical quantity that measures the amount of material of constituent (mass, number of molecules, etc.). Let $c_\alpha$ and $C_\alpha$ be the densities of this quantity in the current and reference configuration. Under the assumption that there are no chemical reactions that convert one constituent into another, the amount of material contained in a part $\mathcal{P}_\alpha$ is equal to that contained in the region $\boldsymbol{\chi}_\alpha(\mathcal{P}_\alpha, t)$ occupied by $\mathcal{P}_\alpha$ at time $t$:

$$\int_{\mathcal{P}_\alpha} C_\alpha(\mathbf{X}) = \int_{\boldsymbol{\chi}_\alpha(\mathcal{P}_\alpha, t)} c_\alpha(\mathbf{x}, t).$$

This yields

$$\phi_\alpha = \frac{c_\alpha}{C_\alpha}.$$

In particular, if $C_\alpha$ does not depend on $X$ in the reference configuration, then $\phi_\alpha$ is proportional to the density $c_\alpha$.

at an intermediate scale, smaller than that at which the theory gives good results (but still larger than that at which the continuum hypothesis breaks down) reveals that the constituents are not at all superposed: they occupy disjoint regions within $\mathcal{S}_\alpha$. Although these regions are so finely mixed that they cannot be distinguished at the macroscopic scale, within each region one can find only one component, whose true specific volume need not be the same as its bulk specific volume.

### 2.3.3 The incompressibility constraint.

For a single constituent, the incompressibility constraint consists in the requirement that the true specific volume be equal to 1. By drawing a cartoon one immediately realizes that:

- for a multicomponent mixture whose constituents are incompressible, the bulk specific volume $\phi_\alpha$ is the fraction of the volume occupied by the $\alpha$–th constituent in a mesoscopic region of space.

Since volume fractions add up to 1, for an incompressible multicomponent mixture the following incompressibility constraint holds:

$$\sum_\alpha \phi_\alpha = 1. \qquad \text{eq:9} \tag{10}$$

**Lemma 2** (Velocity constraint imposed by incompressibility)**.** *Every velocity field consistent with* (10) *must satisfy*

$$\sum_\alpha \left( \phi_\alpha \operatorname{div} \mathbf{v}_\alpha + \operatorname{grad} \phi_\alpha \cdot \mathbf{v}_\alpha \right) = 0. \qquad \text{eq:7} \tag{11}$$

**Remark 1.** One would be tempted to argue from (10) that $\sum_\alpha \grave{\phi}_\alpha = 0$. Note however that the partial derivative in this sum are performed following the individual constituents.

### 2.3.4 The mean velocity.

We define the material derivative of $\varphi$ following the motion of the mixture as

$$\dot{\varphi} := \partial_t \varphi + \operatorname{grad} \varphi \cdot \mathbf{v}, \tag{12}$$

where

$$\mathbf{v} = \sum_\alpha \phi_\alpha \mathbf{v}_\alpha. \qquad \text{eq:8} \tag{13}$$

is the average velocity of the mixture.

lem:1 **Lemma 3.** [1] *Assume that $\varphi$ is continuously differentiable with respect to $\mathbf{x}$ and $t$. Then*

$$\dot{\varphi} = \sum_\alpha \phi_\alpha \overset{\alpha}{\grave{\varphi}},$$

**Remark 2** (The velocity of the mixture)**.** The choice of the weights in (13) appears arbitrary. A better alternative may be to define the average velocity $\mathbf{v}$ of the mixture by asking that

$$\mathbf{T} \cdot \operatorname{grad} \mathbf{v} = \sum_\alpha (\mathbf{T}_\alpha \cdot \operatorname{grad} \mathbf{v}_\alpha + \mathbf{f}_\alpha \cdot \mathbf{v}_\alpha)$$

A question worth further investigation is whether the above equation has solution.

## 2.4 Three formulations of the dissipation principle for a system of superposed continua

### 2.4.1 Partwise and pointwise formulation.

Given a region $\Omega$ let $\Omega_\alpha(t)$ be a time dependent region convecting with the component $\alpha$

$$\Omega_\alpha(t) = \boldsymbol{\chi}_\alpha(\mathcal{P}_\alpha, t),$$

such that

$$\Omega_\alpha(t_0) = \Omega.$$

The dissipation principle dictates that there exists referential state fields $\Psi_\alpha$ satisfying the inequality

$$\sum_\alpha \frac{\mathrm{d}}{\mathrm{d}t}\bigg|_{t=t_0} \int_{\mathcal{P}_\alpha} \Psi_\alpha - \int_\Omega \lambda \sum_\alpha (\phi_\alpha \operatorname{div} \mathbf{v}_\alpha + \operatorname{grad} \phi_\alpha \cdot \mathbf{v}_\alpha) \leq \mathscr{W}_{\mathrm{int}}(\Omega)[\mathbf{v}_1, \ldots, \mathbf{v}_n]$$

for every realizable process and for every region $\Omega$. Here $\lambda$ is the pressure, the Lagrange multiplier associated to the incompressibility constraint (11).

**Proposition 1.** *If the dissipation inequality holds true for every region $\Omega$ and for every process, then the following inequality holds pointwise:*[3]

$$\sum_\alpha \Big( -\phi_\alpha \grave{\Psi}_\alpha + (\mathbf{T}_\alpha + \phi_\alpha \lambda \mathbf{I}) \cdot \operatorname{grad} \mathbf{v}_\alpha + (\mathbf{f}_\alpha + \lambda \operatorname{grad} \phi_\alpha) \cdot \mathbf{v}_\alpha \Big) \geq 0.$$

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[3] Here $\Psi_\alpha$ stands for the Eulerian representation of the specific free energy.

### 2.4.2 Pointwise formulation using spatial densities: the chemical–potential tensor.

On introducing the *spatial* free energy densities

$$\psi_\alpha = \phi_\alpha \Psi_\alpha,$$

and owing to the identities $\grave{\psi}_\alpha = \grave{\phi}_\alpha \Psi_\alpha + \phi_\alpha \grave{\Psi}_\alpha$ and $\grave{\phi}_\alpha = -\phi_\alpha \operatorname{div} \mathbf{v}_\alpha$, we can rewrite the pointwise dissipation inequality as

$$-\sum_\alpha \left( \grave{\psi}_\alpha + \phi_\alpha (\mathbf{K}_\alpha - \lambda \mathbf{I}) \cdot \operatorname{grad} \mathbf{v}_\alpha \right) + \sum_\beta (\mathbf{f}_\beta + \lambda \operatorname{grad} \phi_\alpha) \cdot \mathbf{v}_\alpha \geq 0, \qquad \text{eq:12} \tag{14}$$

where

$$\mathbf{K}_\alpha := \Psi_\alpha \mathbf{I} - \phi_\alpha^{-1} \mathbf{T}_\alpha \qquad \text{eq:34} \tag{15}$$

is called *chemical potential tensor* of the $\alpha$–th constituent.[4]

### 2.4.3 Formulation using spatial control volumes: the total free energy and the boundary flux.

We introduce the total free energy density:

$$\psi = \sum_\alpha \psi_\alpha .$$

**Proposition 2.** *The dissipation inequality is equivalent to*

$$\frac{\mathrm{d}}{\mathrm{d}t} \int_\Omega \psi + \int_{\partial\Omega} \psi_\alpha \mathbf{v}_\alpha \cdot \mathbf{n} \leq \mathscr{W}_{\text{int}}(\Omega)[\mathbf{v}_1, \ldots, \mathbf{v}_n]. \qquad \text{eq:27} \tag{16}$$

The second term on the left–hand side is interpreted as the boundary influx of free energy.

## 2.5 Constitutive equations

### 2.5.1 Partial free energies.

We assume that the referential free energy densitiy of each component $\alpha$ depends on the deformation gradient of the solid component and on the volume fractions of the fluid components:

$$\Psi_\alpha = \widehat{\Psi}_\alpha(\mathbf{F}, \phi_2, \ldots, \phi_N) \equiv \widehat{\Psi}_\alpha(\mathbf{F}, \phi_\beta), \qquad \text{eq:21} \tag{17}$$

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[4] See Eq. 2.42 of the paper [4] by Bowen.

Here and in the following we omit specifying the subscript of the deformation gradient of the solid component:[5]

$$\mathbf{F} \equiv \mathbf{F}_s.$$

As apparent from (17), the free energy density of the $\alpha$–th constituent depends not only on the configuration $\boldsymbol{\chi}_\alpha(\cdot, t)$ of that constituent, but also on the configurations of the other constituents. The corresponding spatial free energy densities obey the following constitutive precriptions:[6]

$$\widehat{\psi}_s(\mathbf{F}, \phi_\beta) = \det \mathbf{F}^{-1} \widehat{\Psi}_s(\mathbf{F}, \phi_\beta), \qquad \widehat{\phi}_\beta(\mathbf{F}, \phi_\beta) = \phi_\beta \widehat{\Psi}_\beta(\mathbf{F}, \phi_\beta).$$

The total free energy of the mixture per unit spatial volume is the sum of the individual energies

$$\psi = \sum_\alpha \widehat{\psi}_\alpha(\mathbf{F}, \phi_\beta) =: \widehat{\psi}(\mathbf{F}, \phi_\beta). \qquad \text{eq:1} \tag{18}$$

It is important to notice that the free energy of the $\alpha$–th component of the mixture depends not only on $\mathbf{F}_\alpha$, but also on the deformation gradients of all other components.

prop:1 **Proposition 3.** *The dissipation inequality* (14) *is satisfied for all admissible processes if and only if*

$$-\sum_\alpha \phi_\alpha \mathbf{K}_\alpha^{(d)} \cdot \operatorname{grad} \mathbf{v}_\alpha + \sum_\alpha \mathbf{f}_\alpha^{(d)} \cdot \mathbf{v}_\alpha \geq 0, \qquad \text{eq:30} \tag{19}$$

eq:33 *where*

$$\mathbf{K}_s^{(d)} = \mathbf{K}_s - \lambda \mathbf{I} + \phi_s^{-1} \frac{\partial \psi}{\partial \mathbf{F}} \mathbf{F}^T, \qquad \text{eq:33a} \tag{20a}$$

$$\mathbf{K}_\beta^{(d)} = \mathbf{K}_\beta - \lambda \mathbf{I} - \frac{\partial \psi}{\partial \phi_\beta} \mathbf{I}, \qquad \textit{for} \qquad \beta \geq 2, \tag{20b}$$

eq:28 *and*

$$\mathbf{f}_s^{(d)} = \mathbf{f}_s + \lambda \operatorname{grad} \phi_s - \operatorname{grad} \psi_s + \frac{\partial \psi}{\partial \mathbf{F}} : \operatorname{grad} \mathbf{F}, \tag{21a}$$

$$\mathbf{f}_\beta^{(d)} = \mathbf{f}_\beta + \lambda \operatorname{grad} \phi_\beta - \operatorname{grad} \psi_\beta + \frac{\partial \psi}{\partial \phi_\beta} \operatorname{grad} \phi_\beta, \quad \beta \geq 2. \tag{21b}$$

*where* $\frac{\partial \Psi}{\partial \mathbf{F}} : \operatorname{grad} \mathbf{F} = \frac{\partial \psi}{\partial F_{ij}} F_{ij,k} \mathbf{e}_k$.

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[5] This will not be source of ambiguities, since it is only the deformation gradient of the solid component that is relevant to our development.

[6] Here the symbol $\phi_\beta$ in the argument of $\widehat{\psi}_s$ and $\widehat{\Psi}_s$ stands for the ordered list $(\phi_\beta)_{\beta \geq 2}$ of the volume fractions of the fluid components.

*Proof (sketch).* A routine computation gives based on (3), (9b), and on the identity

$$\operatorname{grad}\mathbf{v}_s = \dot{\mathbf{F}}\mathbf{F}^{-1},$$

yields[7]

$$\begin{aligned}\sum_\alpha \grave{\psi}_\alpha =& \sum_\alpha \frac{\partial \psi_\alpha}{\partial t} + \sum_\alpha \operatorname{grad}\psi_\alpha \cdot \mathbf{v}_\alpha \\ =& \frac{\partial \psi}{\partial t} + \sum_\alpha \operatorname{grad}\psi_\alpha \cdot \mathbf{v}_\alpha \\ =& \frac{\partial \psi}{\partial \mathbf{F}}\mathbf{F}^T \cdot \operatorname{grad}\mathbf{v}_s - \sum_\beta \phi_\beta \frac{\partial \psi}{\partial \phi_\beta} \operatorname{div}\mathbf{v}_\beta \\ &+ \operatorname{grad}\psi_s \cdot \mathbf{v}_s - \frac{\partial \psi}{\partial \mathbf{F}} \cdot \operatorname{grad}\mathbf{F}[\mathbf{v}_s] \\ &+ \sum_\beta (\operatorname{grad}\psi_\beta - \frac{\partial \psi}{\partial \phi_\beta}\operatorname{grad}\phi_\beta) \cdot \mathbf{v}_\beta.\end{aligned}$$

Substitution into (14) yields the thesis. □

**Remark 3.** We notice that since $\psi = \sum_\alpha \psi_\alpha$ and $\sum_\alpha \phi_\alpha = 1$, the energetic parts of the internal forces, defined by

$$\begin{aligned}\mathbf{f}_s^{(e)} &= -\lambda \operatorname{grad}\phi_s + \operatorname{grad}\psi_s - \frac{\partial \psi}{\partial \mathbf{F}} : \operatorname{grad}\mathbf{F}, \qquad \text{and} \\ \mathbf{f}_\beta^{(e)} &= -\lambda \operatorname{grad}\phi_\beta + \operatorname{grad}\psi_\beta - \frac{\partial \psi}{\partial \phi_\beta}\operatorname{grad}\phi_\beta, \quad \beta \geq 2,\end{aligned} \tag{22}$$

add up to null:

$$\sum_\alpha \mathbf{f}_\alpha^{(e)} = \mathbf{0}. \tag{23}$$

eq:33 **Remark 4.** *The splitting* (24) *can also be written as* $\mathbf{K}_\alpha = \mathbf{K}_\alpha^{(e)} + \mathbf{K}_\alpha^{(d)}$, *with*

$$\mathbf{K}_s^{(e)} = -\phi_s^{-1}\frac{\partial \psi}{\partial \mathbf{F}}\mathbf{F}^T + \lambda \mathbf{I}, \qquad \text{eq:33a} \tag{24a}$$

$$\mathbf{K}_\beta^{(e)} = \frac{\partial \psi}{\partial \phi_\beta}\mathbf{I} + \lambda \mathbf{I}, \qquad \textit{for} \qquad \beta \geq 2, \tag{24b}$$

*the energetic parts of the chemical potential tensors.*

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[7] See endnote [2],
and also endnote [3]

rem:alt **Remark 5** (Alternative expressions for the stresses)**.** We note that, since $\phi_\alpha = 1/\det \mathbf{F}_\alpha$, on letting $\det \mathbf{F}_\alpha = J_\alpha$, we can write

$$\frac{\partial \phi_\alpha}{\partial \mathbf{F}_\alpha} = \frac{\partial J_\alpha^{-1}}{\partial \mathbf{F}_\alpha} = -J_\alpha^{-1}\mathbf{F}_\alpha^{-T} = -\phi_\alpha \mathbf{F}_\alpha^{-T}, \tag{25}$$

hence

$$\frac{\partial(\phi_\alpha \Psi_\alpha)}{\partial \mathbf{F}_\alpha}\mathbf{F}_\alpha^T = \phi_\alpha \frac{\partial \Psi_\alpha}{\partial \mathbf{F}_\alpha}\mathbf{F}_\alpha^T - \phi_\alpha \Psi_\alpha \mathbf{I}. \qquad \text{eq:48} \tag{26}$$

We also notice that if $\Psi_\beta$ depends on $\mathbf{F}_\alpha$ only through the volume fraction $\phi_\alpha$, then

$$\frac{\partial(\phi_\beta \Psi_\beta)}{\partial \boldsymbol{F}_\alpha}\mathbf{F}_\alpha^T = -\phi_\beta \phi_\alpha \frac{\partial \Psi_\beta}{\partial \phi_\alpha}\boldsymbol{I}. \tag{27}$$

eq:53 From these observations, (33) can be given the form

$$\phi_s^{-1}\mathbf{T}_s = \frac{\partial \Psi_s}{\partial \mathbf{F}}\mathbf{F}^T - \left(\lambda + \sum_{\beta \geq 2} \phi_\beta \frac{\partial \Psi_s}{\partial \phi_\beta}\right)\mathbf{I} - \mathbf{K}_s^{(d)}, \qquad \text{eq:36a} \tag{28a}$$

$$\phi_\beta^{-1}\mathbf{T}_\beta = -\left(\lambda + \sum_{\alpha} \phi_\alpha \frac{\partial \Psi_\alpha}{\partial \phi_\beta}\right)\mathbf{I} - \mathbf{K}_\beta^{(d)}, \qquad \beta \geq 2. \tag{28b}$$

In some applications, it is convenient to express the dependence of the free energy of the solid component in the form

$$\widehat{\Psi}_\alpha(\mathbf{F}, \phi_\beta) = \overline{\Psi}_\alpha(\mathbf{F}, \phi_s, \phi_\beta). \tag{29}$$

In these cases, the expression (28) are replaced by

$$\phi_s^{-1}\mathbf{T}_s = \frac{\partial \Psi_s}{\partial \mathbf{F}}\mathbf{F}^T - \left(\lambda + \sum_{\alpha} \phi_\alpha \frac{\partial \overline{\Psi}_\alpha}{\partial \phi_s}\right)\mathbf{I} - \mathbf{K}_s^{(d)}, \tag{30}$$

$$\phi_\beta^{-1}\mathbf{T}_\beta = -\left(\lambda + \sum_{\alpha} \phi_\alpha \frac{\partial \overline{\Psi}_\alpha}{\partial \phi_\beta}\right)\mathbf{I} - \mathbf{K}_\beta^{(d)}, \qquad \beta \geq 2. \tag{31}$$

The scalar field

$$\pi_\alpha = \sum_{\alpha} \phi_\alpha \frac{\partial \overline{\Psi}_\alpha}{\partial \phi_s} \tag{32}$$

is the *osmotic pressure of the* $\alpha$*-th component.*

### 2.5.2 Reduced balance equations.

From definition (15) of the chemical potential tensor we get the expression $\boldsymbol{T}_\alpha = -\phi_\alpha \boldsymbol{K}_\alpha + \psi_\alpha \mathbf{I}$ of the partial stress in terms of chemical potential tensor and partial free energy. Substitution of this expression into (24) yields a set of *reduced constitutive prescriptions* for the stresses: eq:36

$$\mathbf{T}_s = \frac{\partial \psi}{\partial \mathbf{F}} \mathbf{F}^T + \phi_s (\Psi_s - \lambda) \mathbf{I} - \phi_s \mathbf{K}_s^{(d)}, \qquad \text{eq:36a} \tag{33a}$$

$$\mathbf{T}_\beta = -\phi_\beta \frac{\partial \psi}{\partial \phi_\beta} \mathbf{I} + \phi_\beta \left( \Psi_\beta - \lambda \right) \mathbf{I} - \phi_\beta \mathbf{K}_\beta^{(d)}. \tag{33b}$$

These prescriptions, when substituted along with (21) into the equilibrium equations (7) yield eq:37

$$\operatorname{div} \frac{\partial \psi}{\partial \mathbf{F}} \mathbf{F}^T - \phi_s \operatorname{grad} \lambda + \frac{\partial \psi}{\partial \mathbf{F}} : \operatorname{grad} \mathbf{F} + \mathbf{b}_s = \mathbf{f}_s^{(d)} + \operatorname{div} \left( \phi_s \mathbf{K}_s^{(d)} \right) \qquad \text{eq:37a} \tag{34a}$$

$$- \phi_\beta \operatorname{grad} \left( \frac{\partial \psi}{\partial \phi_\beta} + \lambda \right) + \frac{\partial \psi}{\partial \phi_\beta} \operatorname{grad} \phi_\beta + \mathbf{b}_\beta = \mathbf{f}_\beta^{(d)} + \operatorname{div} \left( \phi_\beta \mathbf{K}_\beta^{(d)} \right). \qquad \text{eq:37b} \tag{34b}$$

### 2.5.3 Alternative format for the reduced balance equations.

From the condition $\sum_\alpha \mathbf{f}_\alpha = \mathbf{0}$ (which we recall is a consequence of frame indifference of the internal power) and from (21) we find $\sum_\alpha \mathbf{f}_\alpha^{(d)} = \mathbf{0}$. It is convenient to write both the equilibrium equations and the reduced dissipation inequality in a form that does not involve $\mathbf{f}_s$ explicitly. As to the equilibrium equations, this is done by adding the equations (34b) to (34a) to get:[8] eq:37+

$$\operatorname{div} \left( \frac{\partial \psi}{\partial \mathbf{F}} \mathbf{F}^T + \psi \mathbf{I} - \sum_\beta \phi_\beta \frac{\partial \psi}{\partial \phi_\beta} \right) - \operatorname{grad} \lambda + \mathbf{b} = \operatorname{div} \left( \sum_\alpha \phi_\alpha \mathbf{K}_\alpha^{(d)} \right) \qquad \text{eq:37a+} \tag{35a}$$

$$- \phi_\beta \operatorname{grad} \left( \frac{\partial \psi}{\partial \phi_\beta} + \lambda \right) + \mathbf{b}_\beta = \mathbf{f}_\beta^{(d)} + \operatorname{div} \left( \phi_\beta \mathbf{K}_\beta^{(d)} \right). \tag{35b}$$

The reduced dissipation inequality, on the other hand, is equivalent to

$$- \sum_\alpha \phi_\alpha \mathbf{K}_\alpha^{(d)} \cdot \operatorname{grad} \mathbf{v}_\alpha + \sum_\beta \mathbf{f}_\beta^{(d)} \cdot (\mathbf{v}_\beta - \mathbf{v}_s) \geq 0. \qquad \text{eq:29} \tag{36}$$

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[8] Note that $\frac{\partial \psi}{\partial \mathbf{F}} : \operatorname{grad} \mathbf{F} + \sum_\beta \frac{\partial \psi}{\partial \phi_\beta} \operatorname{grad} \phi_\beta = \operatorname{grad} \psi = \operatorname{div}(\psi \mathbf{I})$.

**Remark 6.** The weighted sum $\psi = \sum_\alpha \phi_\alpha \Psi_\alpha$ represents the free energy per unit volume of the mixture. It is immediately seen that the total Cauchy stress $\mathbf{T} = \sum_\alpha \mathbf{T}_\alpha$ depends only on $\psi$. Indeed, from (33) we have:[9]

$$\mathbf{T} := \sum_\alpha \mathbf{T}_\alpha = \frac{\partial \psi}{\partial \mathbf{F}} \mathbf{F}^T + (\psi - \lambda)\mathbf{I} - \sum_\beta \phi_\beta \frac{\partial \psi}{\partial \phi_\beta} - \sum_\alpha \phi_\alpha \mathbf{K}_\alpha^{(d)}. \tag{37}$$

If we add the partial balances (7) and we use the fact that the internal forces add up to null, we obtain

$$-\operatorname{div} \mathbf{T} = \mathbf{b}, \qquad \text{eq:47} \tag{38}$$

which coincides with (35).

In the case of a body made of a single incompressible constituent, the above equation reduces to

$$\mathbf{T} = \frac{\partial \psi}{\partial \mathbf{F}} \mathbf{F}^T + (\psi - \lambda)\mathbf{I}. \qquad \text{eq:48} \tag{39}$$

In this case the referential and spatial energies coincide, because the Jacobian of the deformation map is equal to 1, and so we recover the standard constitutive equation.

### 2.5.4 Evolution equations.

It is immediate from Proposition 3 that constitutive equations consistent with the
eq:16 dissipation inequality (36) are

$$\mathbf{K}_\alpha^{(d)} = \mathbf{0}, \qquad \text{eq:16a} \tag{40a}$$

$$\mathbf{f}_\beta^{(d)} = \phi_\beta k_\beta (\mathbf{v}_\beta - \mathbf{v}_s), \qquad k_\beta = \widehat{k}_\beta(\phi_2, \ldots, \phi_n). \tag{40b}$$

This choice models a mixture of an incompressible elastic solid and $N-1$ incompressible inviscid fluids. In particular, the chemical potential tensors of the fluids are $\mathbf{K}_\beta = \mu_\beta \mathbf{I}$, where

$$\mu_\beta = -(\lambda + p_\beta), \qquad p_\beta := \frac{\partial \psi}{\partial \phi_\beta}. \tag{41}$$

The fields $p_\beta$ are called *partial pressures.* The following system governing the evolu-
eq:37++ tion of the mixture is arrived at:

$$\operatorname{div}\left( \frac{\partial \psi}{\partial \mathbf{F}} \mathbf{F}^T + \psi \mathbf{I} - \sum_\beta \phi_\beta \frac{\partial \psi}{\partial \phi_\beta} \right) - \operatorname{grad} \lambda + \mathbf{b} = \mathbf{0}, \qquad \text{eq:37a++} \tag{42a}$$

$$k_\beta (\mathbf{v}_\beta - \mathbf{v}_s) = -\operatorname{grad}(p_\beta + \lambda). \qquad \text{eq:37b++} \tag{42b}$$

---

[9] See also Eq. 3.22 of Bowen's paper [4], where the total stress is called the *inner part of the stress* and is denoted by $\mathbf{T}_I$.

A couple of remarks are in order:

- the evolution equations (34) do not depend on how the total free energy $\psi$ splits into its addenda $\psi_\alpha$;
- however, the boundary conditions in terms of stresses depend on such splitting. Thus how one chooses this splitting has relevant physical consequences;

The second remark deserves a further comment. In continuum mechanics a loading environment is modeled by prescribing boundary conditions of traction. These conditions are translated in terms of stress through the Cauchy relation (see (8)), regardless what the constitutive prescription for the stress be. Once the constitutive equation for the free energy is provided, these conditions lead to a precise mathematical statement through a sequence of steps **free of ambiguity**. For a superposition of continua, however, there is ambiguity concerning the expression of the partial stresses because of the manifold of choices for the free energies of the individual components. As a result, the same set of boundary conditions of traction type, will lead to **different mathematical statements** concerning boundary conditions, according to what choice has been mad for the free energies.

### 2.5.5 Ascribing the entire free energy to the solid constituent.

In this case $\psi_\beta = 0$ for all $\beta = 2, \ldots, N$. The total spatial free energy coincides with that of the solid constituent:

$$\psi(\mathbf{F}, \phi_\beta) = \psi_s(\mathbf{F}, \phi_\beta) = \phi_s \Psi_s(\mathbf{F}, \phi_\beta) = (\det\mathbf{F})^{-1} \Psi_s(\mathbf{F}, \phi_\beta).$$

Then

$$\frac{\partial \psi}{\partial \mathbf{F}} \mathbf{F}^T = (\det\mathbf{F})^{-1} \frac{\partial \Psi_s}{\partial \mathbf{F}} \mathbf{F}^T - \psi_s.$$

Therefore, the Cauchy stress of the solid constituent is

$$\mathbf{T}_s = \phi_s \frac{\partial \Psi_s}{\partial \mathbf{F}} \mathbf{F}^T - \phi_s \lambda \mathbf{I}.$$

Moreover, the partial pressures are given by:

$$p_\beta = \phi_s \frac{\partial \Psi_s}{\partial \phi_\beta}$$

and the Cauchy stress of the fluid constituent $\beta$ is

$$\mathbf{T}_\beta = -\phi_\beta (p_\beta + \lambda) \mathbf{I}, \qquad .$$

The total Cauchy stress is therefore:

$$\mathbf{T} = \sum_\alpha \mathbf{T}_\alpha = \phi_s \frac{\partial \Psi_s}{\partial \mathbf{F}} \mathbf{F}^T - \left( \sum_\beta \phi_\beta p_\beta + \lambda \right) \mathbf{I} \qquad \text{eq:18} \tag{43}$$

Note that we can write

$$\mathbf{T}_\beta = -\phi_\beta q_\beta \mathbf{I}, \qquad q_\beta = p_\beta + \lambda.$$

## 2.6 The special case of two constituents with $\psi_\beta = 0$.

### 2.6.1 Spatial description

When the number of fluid constituents reduces to 1, the volumetric constraint (10) yields $\phi_f = 1 - \phi_s$, and hence, because of (11), $\phi_f = (\det\mathbf{F} - 1)/\det\mathbf{F}$. Thus without loss of generality one can assume that $\Psi_s$ does not depend on $\phi_f$:[10]

$$\frac{\partial \Psi_s}{\partial \phi_f} = 0.$$

In this case, one has one more reason to think of the free energy as entirely pertaining to the solid constituent and assume $\psi_f = 0$. In this special case, the constitutive equation (43) delivering the total stress takes the form

$$\mathbf{T} = \phi_s \frac{\partial \Psi_s}{\partial \mathbf{F}} \mathbf{F}^T - \lambda \mathbf{I},$$

and the partial pressure $p_f$ vanishes. The motion equation of the fluid constituent (34b) becomes

$$k_f(\mathbf{v}_f - \mathbf{v}_s) = -\operatorname{grad} \lambda. \qquad \text{eq:19} \tag{44}$$

# 3 Equivalence between different forms of the dissipation inequality

In this section we establish the relation between theories based on interacting continua [4, 5], and the theory depicting the gel as a single continuum [7].

---

[10] If this is not the case, one can introduce the constitutive mapping:

$$\widetilde{\Psi}_s(\mathbf{F}) := \widehat{\Psi}_s\Big(\mathbf{F}, \frac{\det\mathbf{F} - 1}{\det\mathbf{F}}\Big).$$

## 3.1 The dissipation inequality for a two–component mixture.

Again, consider a situation when there is only one fluid constituent and the free energy of the mixture (including the interaction energy) is ascribed entirely to the solid constituent, that is to say, $\psi_f = 0$. In this case, the dissipation inequality for a fixed spatial region $\Omega$ is

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_\Omega \psi_s + \int_{\partial\Omega} \psi_s \mathbf{v}_s \cdot \mathbf{n} \leq \int_\Omega (\mathbf{T}_s \cdot \operatorname{grad} \mathbf{v}_s + \mathbf{T}_f \cdot \operatorname{grad} \mathbf{v}_f + \mathbf{f}_s \cdot \mathbf{v}_s + \mathbf{f}_f \cdot \mathbf{v}_f). \quad \text{eq:20} \tag{45}$$

For the reader's sake we recall the following facts:

- $\psi_s$ denotes the free energy of the solid constituent per unit spatial volume. Such quantity is related to the corresponding free energy density $\Psi_s$ per unit referential volume of the solid constituent by

  $$\psi_s = \phi_s \Psi_s,$$

  where $\phi_s = 1/\det \mathbf{F}$ is the volume fraction of the solid constituent.

- $\mathbf{T}_s$ and $\mathbf{T}_f$ are the partial Cauchy stresses of the solid and of the fluid, and

  $$\mathbf{T} = \mathbf{T}_s + \mathbf{T}_f$$

  is the total stress.

- the fluid stress is $\boldsymbol{T}_f = -\phi_f \lambda \mathbf{I}$, where $\phi_f$ is the fluid volume fraction and $\lambda$ is the Lagrange multiplier associated to the incompressibility constraint.

- $-\mathbf{f}_s$ and $-\mathbf{f}_f$ are the body forces acting on each continuum due to the interaction with the other continuum.

- under the assumption that external body forces vanish, the principle of virtual powers entails a balance equation

  $$-\operatorname{div} \mathbf{T}_\alpha + \mathbf{f}_\alpha = \mathbf{0}$$

  for each constituent $\alpha = 1, 2$.

- invariance of the internal power with respect to superposition of translation fields entails that the interaction forces add up to null: $\mathbf{f}_f + \mathbf{f}_s = \mathbf{0}$, so that the dissipation inequality can be rewritten as

  $$\frac{\mathrm{d}}{\mathrm{d}t}\int_\Omega \psi_s + \int_{\partial\Omega} \psi_s \mathbf{v}_s \cdot \mathbf{n} \leq \int_\Omega (\mathbf{T}_s \cdot \operatorname{grad} \mathbf{v}_s + \mathbf{T}_f \cdot \operatorname{grad} \mathbf{v}_f + \mathbf{f}_f \cdot (\mathbf{v}_f - \mathbf{v}_s)). \quad \text{eq:43} \tag{46}$$

## 3.2 The molar flux and the molar chemical potential.

Now, we perform a sequence of formal manipulations to rewrite the right–hand side of the dissipation inequality:

$$\int_\Omega (\mathbf{T}_s \cdot \operatorname{grad} \mathbf{v}_s + \mathbf{T}_f \cdot \operatorname{grad} \mathbf{v}_f + \mathbf{f}_f \cdot (\mathbf{v}_f - \mathbf{v}_s))$$

$$= \int_\Omega (\mathbf{T}_s + \mathbf{T}_f) \cdot \operatorname{grad} \mathbf{v}_s + \mathbf{T}_f \cdot \operatorname{grad}(\mathbf{v}_f - \mathbf{v}_s) + \mathbf{f}_f \cdot (\mathbf{v}_f - \mathbf{v}_s)$$

(on recalling the identity $\operatorname{div} \mathbf{T}_f = \mathbf{f}_f$ and on setting $\mathbf{T} = \mathbf{T}_s + \mathbf{T}_f$)

$$= \int_\Omega \mathbf{T} \cdot \operatorname{grad} \mathbf{v}_s + \int_{\partial\Omega} \mathbf{T}_f \mathbf{n} \cdot (\mathbf{v}_f - \mathbf{v}_s)$$

(on defining the molar flux of fluid relative to the solid $\mathbf{h} = (\phi_f/v)(\mathbf{v}_f - \mathbf{v}_s)$, where $v$ is the molar volume)

$$= \int_\Omega \mathbf{T} \cdot \operatorname{grad} \mathbf{v}_s + \int_{\partial\Omega} \frac{v}{\phi_f} \mathbf{T}_f \mathbf{n} \cdot \mathbf{h}$$

(on recalling that $\mathbf{T}_f = -\phi_f \lambda \mathbf{I}$ for the fluid constituent)

$$= \int_\Omega \mathbf{T} \cdot \operatorname{grad} \mathbf{v}_s - \int_{\partial\Omega} v\lambda \mathbf{h} \cdot \mathbf{n}$$

(on introducing the molar chemical potential $\mu = v\lambda$)

$$= \int_\Omega \mathbf{T} \cdot \operatorname{grad} \mathbf{v}_s - \int_{\partial\Omega} \mu \mathbf{h} \cdot \mathbf{n}.$$

We have thus proved the following result.

**Proposition 4.** *The dissipation inequality* (46) *is equivalent to*

$$\frac{\mathrm{d}}{\mathrm{d}t} \int_\Omega \psi_s + \int_{\partial\Omega} \psi_s \mathbf{v}_s \cdot \mathbf{n} \le \int_\Omega \mathbf{T} \cdot \operatorname{grad} \mathbf{v}_s - \int_{\partial\Omega} \mu \mathbf{h} \cdot \mathbf{n}. \qquad \text{eq:44} \tag{47}$$

*where, if $v$ the molar volume of the fluid molecules, then*

$$\mathbf{h} = (\phi_f/v)(\mathbf{v}_f - \mathbf{v}_s)$$

*is the* molar flux of fluid relative to the solid, *and*

$$\mu = v\lambda$$

*is the* molar chemical potential of the fluid.

## 3.3 Recovering the dissipation inequality of the homogenized solid

Next, consider a time-dependent spatial region $\Omega(t)$ that convects with the solid:

$$\Omega(t) = \boldsymbol{\chi}_s(\mathcal{P}_s, t) \qquad \text{for some body part } \mathcal{P}_s \text{ of the solid,}$$

and coincides with $\Omega$ at a given time $t_0$:

$$\Omega(t_0) = \Omega.$$

It is standard to establish that, at time $t_0$,

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_\Omega \psi_s + \int_{\partial\Omega} \psi_s \mathbf{v}_s \cdot \mathbf{n} = \frac{\mathrm{d}}{\mathrm{d}t}\int_{\Omega(t)} \psi_s = \int_\Omega \phi_s \dot{\Psi}_s. \tag{48}$$

Thus, the dissipation inequality can be given the form

$$\int_\Omega \phi_s \dot{\Psi}_s \leq \int_\Omega \mathbf{T} \cdot \operatorname{grad} \mathbf{v}_s + \int_{\partial\Omega} \mu \mathbf{h} \cdot \mathbf{n}. \qquad \text{eq:17} \tag{49}$$

Using (49), it is now straightforward to prove the next proposition, which yields the dissipation inequality used in [7], where the mixture is treated as a single solid.

**Proposition 5.** *Satisfaction of the the dissipation inequality* (47) *for every spatial control volume $\Omega$ engaged by the solid component is equivalent to asking that, for each body part $\mathcal{P}$ of the solid,*

$$\int_{\mathcal{P}} \dot{\Psi}_s \leq \int_{\mathcal{P}} \mathbf{T}_R \cdot \operatorname{grad}_R \mathbf{v}_s + \int_{\partial\mathcal{P}} \mu \mathbf{h}_R \cdot \mathbf{n}_R, \tag{50}$$

*where*

$$\mathbf{T}_R = \mathbf{T}\mathbf{F}^\star = (\det \mathbf{F})\mathbf{T}\mathbf{F}^{-\mathsf{T}}, \qquad \mathbf{h}_R = (\mathbf{F}^\star)^\mathsf{T}\mathbf{h} = (\det \mathbf{F})\mathbf{F}^{-1}\mathbf{h}. \tag{51}$$

*are, respectively, the referential stress and the referential flux,* $\operatorname{grad}_R$ *denotes the referential gradient and* $\mathbf{n}_R$ *is the outward unit normal to* $\mathcal{P}$.

## 3.4 Referential form of the motion equation of the fluid constituent.

Recalling the identity

$$\operatorname{grad}_R \lambda = \mathbf{F}^T \operatorname{grad} \lambda.$$

we can write the spatial form of the motion equation (44) as

$$-\operatorname{grad}_R \lambda - k_f(\det \mathbf{F})^{-1}\mathbf{F}^T\mathbf{F}\mathbf{h}_R = \mathbf{0}.$$

This yields the following relation for the referential flux:

$$\mathbf{h}_R = -k_f^{-1}(\det \mathbf{F})(\mathbf{F}^T\mathbf{F})^{-1}\operatorname{grad}_R \lambda = -(v k_f)^{-1}(\det \mathbf{F})(\mathbf{F}^T\mathbf{F})^{-1}\operatorname{grad}_R \mu. \quad \text{eq:42} \tag{52}$$

This relation that agrees with the constitutive equation for the flux adopted in [7]. There is an important difference, however: according to [7], (52) is a constitutive equation. In our case, it is the consequence of an equilibrium equation.

## 4 Modeling polymer gels as porous materials

We would like to use the format for poromechanics developed in [**AdC**] to reformulate the theory of polymer gels in such a way that the Darcy law emerges as a combination of a balance equation and a constitutive equation. To this effect our first goal is to see how the mathematical model for polymer gel relates to that for saturated porous medium whose solid skeleton is incompressible. To this aim, a handful of kinematical considerations are in order.

**The swelling constraint.** We suppose that in the state that we take as reference the concentraion is $c^*$, measured in moles per unit volume. Accordingly the number of moles of solvent in an elementary volume $dV$ in the reference configuration is $dN = c^* dV$. Thus, if we denote by $\Omega$ the molar volume of the solvent, then $dV^f = \Omega dN = c^* dV$ is the volume occupied by solvent molecules within the volume $dV$. The remaining part of the volume is occupied by the solid so that

$$dV^s = dV - dV^f \quad \text{eq:32} \tag{53}$$

is the volume occupied by the solid network. When the gel goes in its current state, the volume $dV$ is mapped into the elementary volume

$$dv = \det(\boldsymbol{F})dV, \quad \text{eq:38} \tag{54}$$

and the referential concentration can change to a new value $c$. The number of solvent moles contained in $dv$ is $dn = c dV$, hence the total volume occupied by the fluid component contained in $dv$ is

$$dv^f = \Omega c dV. \quad \text{eq:31} \tag{55}$$

Now, $dv^s = dv - dv^f$ is the volume occupied by the solid component. Since the solid component is incompressible, we have $dv^s = dV^s$, hence $dv - dv^f = dV - dV^f$, which implies, by (55), (54), and (53), that

$$\det \boldsymbol{F} = 1 + \Omega(c - c^*), \tag{56}$$

an condition that goes by the name of "swelling constraint".

Note that, since $dv^s = dv - \Omega c dV$ and $dV^s = (1 - \Omega c)dV$, we can think of a gel as a saturated porous material whose pores are entirely occupied by the fluid. Accordingly the quantity

$$\varphi = \Omega c \tag{57}$$

would be, in poromechanics, the volume currently occupied by the pores that are originally contained in a unit reference volume. Likewise $\varphi^* = \Omega c^*$ would be the porosity in the reference state.

### 4.1 Reformulation

At this point, we ask the following question: is it possible to reformulate the equations governing polymer gels so that the Darcy law emerges as a combination of. Moreover, what is the connection between the principle of virtual work as stated in the theory of mixtures and the principle of virtual work in AdC poromechanics?

### 4.2 Boundary conditions

COME VENGONO ASSEGNATE LE CONDIZIONI AL CONTORNO IN TERMINI DI SFORZI?

### 4.3 A one dimensional example

tappo tra due regioni aventi differente pressione

********************************** STOP HERE STOP HERE ************************************

## 5 The theory of Doi

Doi regards the gel as a mixture of a solid and a fluid. Each constituent has a peculiar velocity.

Doi uses a variational approach, based on writing a Rayleighian functional that takes into account free energy and dissipation:

$$\mathcal{R}(\mathbf{v}_s, \mathbf{v}_f) = \mathcal{D}(\mathbf{v}_s, \mathbf{v}_f) + D\mathcal{E}(\mathbf{v}_s, \mathbf{v}_f)$$

Here $\mathbf{v}_s$ and $\mathbf{v}_f$ denote the velocities of, respectively, the solid and the fluid constituent of the mixture.

Consider a bounded region $V$ occupied by the mixture, and suppose that the velocities of the constituents are $\mathbf{v}_1$ and $\mathbf{v}_2$. The Flory-Huggins energy is the sum

$$\mathcal{E} = \mathcal{E}_{\mathsf{str}} + \mathcal{E}_{\mathsf{int}}$$

of a strain energy

$$\mathcal{E}_{\mathsf{str}} = \int_V \frac{1}{\det \mathbf{F}_1} \widehat{W}(\mathbf{F}_1)$$

and an interaction energy

$$\mathcal{E}_{\mathsf{int}} = \int_V h(\phi_1, \phi_2),$$

where $\phi_\alpha = \frac{1}{\det \boldsymbol{F}_\alpha}$ are the volume fractions. The time derivative of the strain energy is

$$\dot{\mathcal{E}}_{\mathsf{str}} = \int_V -\frac{1}{(\det \mathbf{F}_1)^2} \widehat{W}(\mathbf{F}_1)\mathbf{F}_1^\star \cdot \mathbf{F}_1' + \frac{1}{\det \mathbf{F}_1} D\widehat{W}(\mathbf{F}_1) \cdot \mathbf{F}_1',$$

where $\mathbf{F}_1'$ is the time derivative holding the position in space $x$ fixed and $\mathbf{F}_1^\star = (\det \mathbf{F}_1)\mathbf{F}_1^{-T}$. The material time derivative of the deformation gradient is

$$\dot{\mathbf{F}}_1 = \mathbf{F}_1' + \mathrm{grad}\mathbf{F}_1\, \mathbf{v}_1.$$

We recall that $\dot{\mathbf{F}}_1\mathbf{F}_1^{-1} = \operatorname{grad}\mathbf{F}_1$. Thus,

$$\begin{aligned}
\dot{\mathcal{E}}_{\mathsf{str}} &= \int_V \left(-\frac{1}{\det\mathbf{F}_1}\widehat{W}(\mathbf{F}_1)\mathbf{F}_1^{-T} + \frac{1}{\det\mathbf{F}_1}D\widehat{W}(\mathbf{F}_1)\right)\cdot{\mathbf{F}_1}' \\
&= \int_V \left(-\frac{1}{\det\mathbf{F}_1}\widehat{W}(\mathbf{F}_1)\mathbf{F}_1^{-T} + \frac{1}{\det\mathbf{F}_1}D\widehat{W}(\mathbf{F}_1)\right)\cdot\dot{\mathbf{F}}_1 - \int_V \left(-\frac{1}{\det\mathbf{F}_1}\widehat{W}(\mathbf{F}_1)\mathbf{F}_1^{-T} + \frac{1}{\det\mathbf{F}_1}D\widehat{W}(\mathbf{F}_1)\right) \\
&= \int_V \left(-\frac{1}{\det\mathbf{F}_1}\widehat{W}(\mathbf{F}_1)\mathbf{I} + \frac{1}{\det\mathbf{F}_1}D\widehat{W}(\mathbf{F}_1)\mathbf{F}_1^T\right)\cdot\dot{\mathbf{F}}_1\mathbf{F}_1^{-1} - \int_V \Bigg(-\frac{1}{\det\mathbf{F}_1}\widehat{W}(\mathbf{F}_1)\mathbf{F}_1^{-T} + \frac{1}{\det\mathbf{F}_1}D\widehat{W}(\mathbf{F} \\
&= -\int_V \frac{1}{\det\mathbf{F}_1}\widehat{W}(\mathbf{F}_1)\operatorname{div}\mathbf{v}_1 + \int_V \mathbf{T}\cdot\operatorname{grad}\mathbf{v}_1 - \int_V \left(-\frac{1}{\det\mathbf{F}_1}\widehat{W}(\mathbf{F}_1)\mathbf{F}_1^{-T} + \frac{1}{\det\mathbf{F}_1}D\widehat{W}(\mathbf{F}_1)\right)\cdot\operatorname{grad} \\
&= -\int_{\partial V} \frac{1}{\det\mathbf{F}_1}\widehat{W}(\mathbf{F}_1)\mathbf{v}_1\cdot\mathbf{n} + \int_V \operatorname{grad}\left(\frac{1}{\det\mathbf{F}_1}\widehat{W}(\mathbf{F}_1)\right)\cdot\mathbf{v}_1 \\
&\quad + \int_V \mathbf{T}\cdot\operatorname{grad}\mathbf{v}_1 - \int_V \left(-\frac{1}{\det\mathbf{F}_1}\widehat{W}(\mathbf{F}_1)\mathbf{F}_1^{-T} + \frac{1}{\det\mathbf{F}_1}D\widehat{W}(\mathbf{F}_1)\right)\cdot\operatorname{grad}\mathbf{F}_1\,\mathbf{v} \\
&= -\int_{\partial V} \frac{1}{\det\mathbf{F}_1}\widehat{W}(\mathbf{F}_1)\mathbf{v}_1\cdot\mathbf{n} + \int_V \left(-\frac{1}{\det\mathbf{F}_1}\widehat{W}(\mathbf{F}_1)\mathbf{F}_1^{-T} + \frac{1}{\det\mathbf{F}_1}D\widehat{W}(\mathbf{F}_1)\right)\cdot\operatorname{grad}\mathbf{F}_1\,\mathbf{v} \\
&\quad + \int_V \mathbf{T}\cdot\operatorname{grad}\mathbf{v}_1 - \int_V \left(-\frac{1}{\det\mathbf{F}_1}\widehat{W}(\mathbf{F}_1)\mathbf{F}_1^{-T} + \frac{1}{\det\mathbf{F}_1}D\widehat{W}(\mathbf{F}_1)\right)\cdot\operatorname{grad}\mathbf{F}_1\,\mathbf{v} \\
&= -\int_{\partial V} \frac{1}{\det\mathbf{F}_1}\widehat{W}(\mathbf{F}_1)\mathbf{v}_1\cdot\mathbf{n} + \int_V \mathbf{T}\cdot\operatorname{grad}\mathbf{v}_1
\end{aligned}$$

A similar result can be arrived at through the following calculation. We define $w = \widehat{w}(\mathbf{F}_1) = \frac{1}{\det\mathbf{F}_1}\widehat{W}(\mathbf{F}_1)$. Then

$$\begin{aligned}
\dot{\mathcal{E}}_{\mathsf{str}} &= \int_V D\widehat{w}(\mathbf{F}_1)\cdot\mathbf{F}_1' \\
&= \int_V D\widehat{w}(\mathbf{F}_1)\cdot(\dot{\mathbf{F}}_1 - \operatorname{grad}\mathbf{F}_1\,\mathbf{v}_1) \\
&= \int_V D\widehat{w}(\mathbf{F}_1)\cdot\dot{\mathbf{F}}_1 - \operatorname{grad}w\cdot\mathbf{v}_1 \\
&= \int_V D\widehat{w}(\mathbf{F}_1)\mathbf{F}_1^T\cdot\operatorname{grad}\mathbf{v}_1 + w\operatorname{div}\mathbf{v}_1 - \int_{\partial V} w\mathbf{v}_1\cdot\mathbf{n} \\
&= \int_V \frac{1}{\det\mathbf{F}_1}D\widehat{W}(\mathbf{F}_1)\mathbf{F}_1^T\cdot\operatorname{grad}\mathbf{v}_1 - \int_{\partial V}\frac{1}{\det\mathbf{F}_1}D\widehat{W}(\mathbf{F}_1)\mathbf{v}_1\cdot\mathbf{n}
\end{aligned}$$

**Lemma 4.** *For an incompressible mixture the volume fractions $\phi_\alpha$ and the spatial velocity fields $\mathbf{v}_\alpha$ satisfy the following identity*

$$\partial_t\phi_\alpha + \operatorname{div}(\phi_\alpha\mathbf{v}_\alpha) = 0. \qquad \text{eq:6} \qquad (58)$$

*Equivalently,*

$$\dot{\phi}_\alpha + \phi_\alpha \operatorname{div} \mathbf{v}_\alpha = 0. \tag{59}$$

*Proof.* The thesis follows on noting that for an incompressible mixture volume fractions are proportional to densities (see (11)). ☐

Differentiation of (10) and use of (58) yields the following constraint on the velocity field:

$$\sum_{\alpha=1}^{n} \left(\phi_\alpha \operatorname{div} \mathbf{v}_\alpha + \operatorname{grad} \phi_\alpha \cdot (\mathbf{v}_\alpha - \mathbf{v}_1)\right) = 0. \qquad \text{eq:10} \tag{60}$$

**Lemma 5.** *Let the time-dependent velocity field* $\boldsymbol{v} = \boldsymbol{v}(x,t)$ *be continuously differentiable and let the* $\Psi = \widehat{\Psi}(\phi)$ *where* $\widehat{\Psi}$ *is a continuously differentiable function. Then*

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_V \phi\Psi = \int_V \phi\dot{\Psi} - \int_{\partial V} \phi\Psi\mathbf{v}\cdot\mathbf{n}$$

## 6 The hosmotic pressure

Consider a situation when there is only one constituent whose volumetric free energy is $\psi = \widehat{\psi}(\phi)$, where $\phi$ is the volume fraction. Suppose that the constituent occupies a region $\Omega$. The time variation of the free energy is

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\int_\Omega \psi &= \int_\Omega \widehat{\psi}'(\phi)\phi' \\ &= -\int_\Omega \widehat{\psi}'(\phi)\left(\phi \operatorname{div}\mathbf{v} + \operatorname{grad}\phi\cdot\mathbf{v}\right) \\ &= -\int_\Omega \left(\psi'\phi \operatorname{div}\mathbf{v} + \operatorname{grad}\psi\cdot\mathbf{v}\right) \\ &= -\int_\Omega (\psi'\phi - \psi)\operatorname{div}\mathbf{v} - \int_{\partial\Omega}\psi\mathbf{v}\cdot\mathbf{n}.\end{aligned} \tag{61}$$

Consequently, the following identity holds

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_\Omega \psi + \int_{\partial\Omega}\psi\mathbf{v}\cdot\mathbf{n} = -\int_\Omega p \operatorname{div}\mathbf{v}, \tag{62}$$

where $p = \phi\psi' - \psi$ is the hosmotic pressure.

Now, the question is how it would be possible to generalize this calculation when there is more than one diffusing species. A possibility is the following:

Let $\psi = \widehat{\psi}(\phi_1, \phi_2)$. Then

$$
\begin{aligned}
\frac{\mathrm{d}}{\mathrm{d}t}\int_\Omega \psi &= \int_\Omega \psi_{,\alpha}\phi'_\alpha \\
&= -\int_\Omega (\psi_{,\alpha}\phi_\alpha \operatorname{div} \mathbf{v}_\alpha + \psi_{,\alpha} \operatorname{grad} \phi_\alpha \cdot \mathbf{v}_\alpha)
\end{aligned}
$$

Note that here we cannot write $\psi_{,\alpha} \operatorname{grad} \phi_\alpha \cdot \mathbf{v}_\alpha = \operatorname{grad} \psi \cdot \mathbf{v}_\alpha$. However, we can continue the calculation as follows:

$$
\begin{aligned}
&= -\int_\Omega (\psi_{,\alpha}\phi_\alpha \operatorname{div} \mathbf{v}_\alpha + \psi_{,\alpha} \operatorname{grad} \phi_\alpha \cdot \mathbf{v}_1 + \psi_{,2} \operatorname{grad} \phi_2 \cdot (\mathbf{v}_2 - \mathbf{v}_1)) \\
&= -\int_\Omega (\psi_{,\alpha}\phi_\alpha \operatorname{div} \mathbf{v}_\alpha + \operatorname{grad} \psi \cdot \mathbf{v}_1 + \psi_{,2} \operatorname{grad} \phi_2 \cdot (\mathbf{v}_2 - \mathbf{v}_1)) \\
&= -\int_\Omega (\psi_{,1}\phi_1 \operatorname{div} \mathbf{v}_1 + \psi_{,2}\phi_2 \operatorname{div} \mathbf{v}_2 + \operatorname{grad} \psi \cdot \mathbf{v}_1 + \psi_{,2} \operatorname{grad} \phi_2 \cdot (\mathbf{v}_2 - \mathbf{v}_1)) \\
&= -\int_\Omega (\psi_{,1}\phi_1 - \psi) \operatorname{div} \mathbf{v}_1 + \psi_{,2}\phi_2 \operatorname{div} \mathbf{v}_2 + \psi_{,2} \operatorname{grad} \phi_2 \cdot (\mathbf{v}_2 - \mathbf{v}_1)) - \int_{\partial\Omega} \psi \mathbf{v}_1 \cdot \mathbf{n}.
\end{aligned}
$$

The scalar field $p = \psi_{,1}\phi_1 - \psi$ is interpreted as the hosmotic pressure of the first constituent.

### 6.0.1 The dissipation inequality of Green and Naghdi

Green and Naghdi [9] do not consider a partition of the free energy into contribution from the individual constituents. Instead, they assume that the mixtures is endowed with a specific free energy $\Psi$ per unit mass and write the following dissipation inequality

$$
\frac{\mathrm{d}}{\mathrm{d}t}\int_\Omega \psi + \int_{\partial\Omega} \psi \mathbf{v} \cdot \mathbf{n} \tag{63}
$$

where $\mathbf{v} = \sum_{\alpha=1}^{n} \phi_\alpha \mathbf{v}_\alpha$ is the mean velocity of the mixture.

**Remark 7.** ***** TO FIX ****

Let $\widehat{\Psi}$ denote the free energy per unit mass of an elastic fluid. The energy per unit volume

$$
\mu\dot{\varrho} = \widehat{\psi}'(\varrho)\dot{\varrho} = (\widehat{\Psi}(\varrho) + \varrho\widehat{\Psi}'(\varrho))\dot{\varrho} = -(\Psi - p/\varrho)\varrho \operatorname{div} \mathbf{v} = -\varrho(\Psi\mathbf{I} - p/\varrho\mathbf{I}) \cdot \operatorname{grad} \mathbf{v} = -\varrho\mathbf{K} \cdot \operatorname{grad} \mathbf{v}.
$$

The tensor $\mathbf{K}$ is referred to as the chemical potential tensor. For a solid, the chemical potential tensor is defined as $\mathbf{K} = \Psi\mathbf{I} - \mathbf{T}/\varrho$.

**Remark 8.** One can define the referential free energy of the mixture by

$$\psi = \sum_\alpha \psi_\alpha = \sum_\alpha \phi_\alpha \Psi_\alpha .$$

In generaal it is not true that $\dot\psi = \sum_\alpha \phi_\alpha \dot\Psi_\alpha$. However, this is the case if the $\Psi_\alpha$ are all the same, that is, when $\psi_\alpha = \phi_\alpha \psi$.

**Lemma 6.**

$$\sum_\alpha \varrho_\alpha D_t^\alpha \Psi_\alpha = \varrho \dot\Psi .$$

## 7 The equation governing the motion of the interacting continua

According to Bowen, the equations governing the evolution of the mixture are the following:
1) A set of balance equations

$$\operatorname{div}\mathbf{T}_\alpha + \mathbf{f}_\alpha = 0, \qquad \alpha = 1, \ldots, n \qquad \textit{eq:2} \tag{64}$$

each involving a partial stress $\mathbf{T}_\alpha$ and an internal force $\mathbf{f}_\alpha$ of the $\alpha$–th constituent. The partial stresses model the interaction between parts of each constituent, whereas the internal forces $\mathbf{f}_\alpha$ represent the interaction forces between the $\alpha$–th constituent and the remaining constituents.
2) The constitutive equation

$$\mathbf{T}_1 = -\lambda\phi_1\mathbf{I} + \psi_1\mathbf{I} + \frac{\partial\psi_1}{\partial\mathbf{F}}\mathbf{F}^T, \qquad \textit{eq:3} \tag{65}$$

which states that the partial stress $\mathbf{T}_1$ of the solid constituent depends, up to a undetermined multiplier $\lambda$, on the deformation gradient $\mathbf{F}$ thorough the derivative of the referential strain energy $\widehat{W}(\mathbf{F})$.
3) The set of constitutive equations

$$\mathbf{T}_\alpha = \psi_\alpha\mathbf{I} - \phi_\alpha(f_\alpha + \lambda)\mathbf{I}, \qquad f_\alpha = \psi_{,\alpha}, \qquad \alpha = 2\ldots n$$

ruling the partial stresses of the fluid constituents.
4) A set of constitutive equations governing the internal forces

$$\mathbf{f}_\alpha = (f_\alpha + \lambda)\operatorname{grad}\phi_\alpha - \operatorname{grad}\psi_\alpha + \mathbf{p}_\alpha^{\mathsf{diss}}, \qquad \textit{eq:4} \tag{66}$$

with $\mathbf{p}_\alpha^{\mathsf{diss}}$ obeying the dissipation inequality

$$\sum_{\alpha=1}^{n} \mathbf{p}_\alpha^{\mathsf{diss}} \cdot \mathbf{v}_\alpha \geq 0.$$

**Remark 9.** *The balance equations and the invariance requirement that the partial stress and the internal forces must obey can be obtained by introducing the power expended within a region $V$ occupied by the mixture:*

$$\mathcal{W}_{\rm int}(V) = \int_V (\mathbf{T}_\alpha \cdot \operatorname{grad} \mathbf{v}_\alpha + \mathbf{f}_\alpha \cdot \mathbf{v}_\alpha)\,.$$

*Imposing that the internal power vanishes for all possible velocities, we obtain the balance equations. On imposing Leibnitzian invariance of the internal power we obtain that the total stress is symmetric*

$$\boldsymbol{T} := \sum_\alpha \mathbf{T}_\alpha \in \mathrm{Sym}$$

*and the the internal forces add up to null:*

$$\sum_\alpha \mathbf{f}_\alpha = 0.$$

**Remark 10.** The constitutive equation governing the partial stress of the solid constituent may appear odd, since it involves the value of the free energy $\psi_\alpha$, besides its derivative with respect to $\mathbf{F}_\alpha$. To resolve this seemingly strange fact, one must remember that the field $\psi_1 = \phi_1 \Psi_1 = \frac{1}{\det \mathbf{F}} \Psi_1$ represents the energy of the elastic constituent per unit volume in the current configuration. A manipulation of the constitutive equation for $\mathbf{T}_1$ allows us to write the constitutive equation in terms of the referential free energy density $\Psi_1$:

$$\mathbf{T}_1 = -\lambda \phi_1 \mathbf{I} + \phi_1 \frac{\partial \Psi_1}{\partial \mathbf{F}} \mathbf{F}^T,$$

that governs the stress in a hyperelastic solid. It is worth noticing, in addition, that the partial stresses are determined up to a multiplicative constant $\lambda$, and that the total stress

$$\mathbf{T} := \sum_{\alpha=1}^{n} \mathbf{T}_\alpha$$

is given by

$$\mathbf{T} = -\lambda \mathbf{I} + \phi_1 \frac{\partial \Psi_1}{\partial \mathbf{F}} \mathbf{F}^T + \sum_{\alpha=2}^{n} (\psi_\alpha + f_\alpha) \mathbf{I}$$

**Remark 11.** Clearly, for a given $\psi$, there are several choices of lists of $\Psi_\alpha$ that produce the same weighted sum. It is interesting to note that,

**Remark 12.** *Note that, the constraint* $\sum_\alpha \phi_\alpha = 1$ *does not imply that* $\sum_\alpha \frac{D_\alpha \phi_\alpha}{D_\alpha t} = 0$.

The partition (18) of the free energy into different constituents provides an arbitrary gauge. Such gauge does not affect the evolution equations governing the system. In fact, the combination of the balance equation (64) with the constitutive prescriptions

# 8 Truesdell's theory of interacting continua

# 9 The inapplicability of mixture theory

As an example of the set of theories relying on the model of interacting continua, we examine more carefully the paper [5]. Our choice falls upon that paper because one of the key steps it contains puts into perspective the danger of a blind use of mixture theory in the modeling of gels.

A key feature of the theory of interacting continua is that it allows distinct bodies to engage the same region of space, at variance with what is taught in basic Continuum Mechanics. One of the consequences of this fact is that at each point in space, the information content needed to describe the state of the system (velocity, mass density, etc) must be replicated for each constituent. In particular, in applications to gels, at each point of the region occupied by the "mixture", a velocity of the solid $\mathbf{v}_s$ and a velocity of the fluid $\mathbf{v}_f$ are defined. Likewise, a density $\varrho_s$ of the solid and a density $\varrho_s$ of the fluid are defined.

**Densities and velocities.** Although more sophisticated mixture theories allow for conversion of one constituent into another, in application to gels there is no chemical reaction between constituents, and it comes with no surprise that densities and velocities obey conventional mass balance laws separately for each constituent, namely,[11]

$$\grave{\varrho}_\alpha + \varrho_\alpha \operatorname{div} \mathbf{v}_\alpha = 0, \qquad \alpha = s, f, \qquad \text{eq:39} \qquad (67)$$

where the grave accent over a field with subscript $\alpha$ denotes the convective derivative taken with respect to the velocity $\mathbf{v}_\alpha$ of the $\alpha$–th constituent, namely, $\grave{\varrho}_\alpha = \frac{\partial \varrho_\alpha}{\partial t} + \mathbf{v}_\alpha \cdot \operatorname{grad} \varrho_\alpha$.

---

[11] Henceforth we avoid specifying the typographical range of the index $\alpha$, which is undestood to be the set {"$s$", "$f$"}.

Although the laws obeyed by the mass-density fields $\varrho_\alpha$ are the same as in standard continuum mechanics, their physical interpretation is subtle. This point is better understood when the incompressiblity of each constituent of the mixture comes into play. This assumption, which we make henceafter, is actually not suggested by pedagogical considerations, but dictated by practical convenience, since the constituents of a gel are typically a rubber and a liquid.

**Incompressible mixtures, true densities and volume fractions.** In the case of a single continuum, incompressibility is equivalent to the density being constant, both in space and time, or, equivalently, that the velocity field be divergenceless. However, for a superposition of continua the relative amount of a constituent with respect to the other may change from one point to another and we cannot expect to be right that the density of each constituent be separately constant. Instead, the correct assumption is that there exist two material constants $\gamma_s$ and $\gamma_f$, carrying the dimensions of mass density, such that

$$\frac{\varrho_s}{\gamma_s}+\frac{\varrho_f}{\gamma_f}=1. \qquad \text{eq:40} \tag{68}$$

In the absence of one of the two constituents, for example if there are no solid particles and $\varrho_s=0$, the incompressibility condition (68) reduces to $\varrho_f=\gamma_f$. Thus, accoding to (68), $\gamma_f$ is to be interpreted as the density of the unmixed fluid. Similar considerations apply to the solid, and justify the name *true densities* for the constants $\gamma_\alpha$.

If introduce the *volume fractions* $\phi_\alpha=\varrho_\alpha/\gamma_\alpha$, then the densities $\varrho_\alpha$ are related to their true counterparts by

$$\varrho_\alpha=\phi_\alpha\gamma_\alpha. \tag{69}$$

and (68) becomes a seemilgly trivial statement: that the sum of the volume fractions of all constituents should be equal to 1:

$$\phi_s+\phi_f=1. \qquad \text{eq:46} \tag{70}$$

Not only volume fractions allow to write the incompressibility constraint in a compact fashion, but they play a prominent role when it comes to the energetics of a gel. Since, as we have seen, the information content of volume fractions is the same as that of the densities for incompressible mixtures, it turns out to be convenient to get rid of mass densities and retain all mass balance equations in terms of volume fractions:

$$\grave{\phi}_\alpha+\phi_\alpha\,\mathrm{div}\,\mathbf{v}_\alpha=0. \qquad \text{eq:39} \tag{71}$$

**Partial stresses.** The existence of more than one velocity at each point goes along the existence of more than one stress tensor: each continuum has its own stress, which obeys its own equilibrium equation. In the case of a gel, we have two balance equations:

$$\gamma_\alpha \phi_\alpha \grave{\mathbf{v}}_\alpha = \operatorname{div} \mathbf{T}_\alpha + \mathbf{f}_\alpha. \qquad \text{eq:41} \tag{72}$$

Although typographically the balance equation (72) is the same as in standard continuum theories, it has the specific feature that the body force $\mathbf{f}_\alpha$ can be internal to the mixture, that is, it incorporates the interaction between the $\alpha$–th component an the other one. Thus, at variance with standard continuum mechanics, whereby the interaction betweem different bodies is a reactive contact forces localized at their common boundaries, in the theory of superposed continua the interaction between the constituents is *diffused* within the common spatial region they occupy.

**Constitutive equations.** For a thermodynamical process involving the superposition of an incompressible elastic solid and an incompressible fluid, the relevant state variables are the deformation gradient $\mathbf{F}_s$ of the solid component and the volume fraction $\phi_f$ of the fluid component. It is convenient, when writing the expressions of the free energy, to make explicit use of the volume fraction of the solid component, which is related to the deformation gradient by

$$\phi_s = \frac{1}{\det \mathbf{F}_s}. \tag{73}$$

According to the Flory-Huggins theory, the totale *free energy per unit current volume* of a gel is the sum of a *strain energy*:

$$\psi^{(\mathrm{str})} = \phi_s \frac{G}{2}(|\mathbf{F}_s|^2 - 3), \qquad \text{eq:49} \tag{74}$$

and a *configurational energy*:

$$\boxed{\psi^{(\mathrm{int})} = \frac{kT}{\Omega}\left(\frac{\chi}{2}\phi_s\phi_f + \frac{1}{N_s}\phi_s \log\phi_s + \frac{1}{N_s}\phi_f \log\phi_f\right).} \qquad \text{eq:50} \tag{75}$$

Now, when willing to fit the constitutive equations (74) and (75) into the apparatus of mixture theory, we face a conceptual issue. Indeed, the dissipation inequality of mixture theory has the following format:

$$-\sum_\alpha \phi_\alpha \grave{\Psi}_\alpha + \mathbf{T}_\alpha \cdot \operatorname{grad} \mathbf{v}_\alpha - \mathbf{f}_\alpha \cdot \mathbf{v}_\alpha \geq 0. \qquad \text{eq:45} \tag{76}$$

The fields $\Psi_\alpha$, called *referential free energies*, represent primitive quantities, and must be prescribed by constitutive specifications through functions $\widehat{\Psi}_\alpha$ of the relevant state variables, namely, $\Psi_s = \widehat{\Psi}_s(\mathbf{F}_s, \phi_f)$ and $\Psi_f = \widehat{\Psi}_f(\mathbf{F}_s, \phi_f)$.

The weighted sum

$$\psi := \sum_\alpha \phi_\alpha \Psi_\alpha \qquad \text{eq:51} \tag{77}$$

represents the total spatial free energy of the mixture. Thus, when applying mixture theory to a gel, physics dictates that the total energy be coincident with the sum of the strain and interaction energy:

$$\psi = \psi^{(\mathrm{str})} + \psi^{(\mathrm{int})}. \tag{78}$$

The choice made in the paper [5] is motivated by the following observations. First of all, the total free energy is the sum of terms that depend separately on $\mathbf{F}_s$ (possibly through its determinant $J_s = \phi_s^{-1}$) and $\phi_f$, with the exception of the first addendum between brackets on the right–hand side of (75). However, since the volume fractions add up to 1 this term can be manipulated as follows:

$$\frac{\chi}{2}\phi_s\phi_f = \frac{\chi}{2}(\phi_s + \phi_s)\phi_s\phi_f = \frac{\chi}{2}\phi_s\phi_f^2 + \frac{\chi}{2}\phi_f\phi_s^2, \tag{79}$$

as a result, the total free energy can be given the form of the weighted sum (77) provided we set

$$\begin{aligned}
\Psi_s &= W(\mathbf{F}_s) + \frac{kT}{\Omega}\left(\frac{1}{N_s}\log\phi_s + \frac{\chi}{2}\phi_f^2\right) =: \overline{\Psi}_s(\mathbf{F}_s, \phi_s, \phi_f),\\
\Psi_f &= \frac{kT}{\Omega}\left(\frac{1}{N_f}\log\phi_f + \frac{\chi}{2}\phi_s^2\right) =: \overline{\Psi}_f(\phi_s, \phi_f).
\end{aligned} \tag{80}$$

Now, a consequence of the above constitutive choice is the following expression of the stresses, which we derive using the results in Remark 5:

$$\begin{aligned}
\mathbf{T}_s &= \phi_S \frac{\partial\overline{\Psi}_s}{\partial\mathbf{F}_s}\mathbf{F}_s^T - (\phi_s\lambda + \pi_s)\mathbf{I},\\
\mathbf{T}_f &= -(\phi_f\lambda + \pi_f)\mathbf{I},
\end{aligned} \tag{81}$$

where $\pi_s$ and $\pi_f$ are the hosmotic pressures, given by

$$\pi_\alpha = -\phi_\alpha \sum_{\beta=f,s} \phi_\beta \frac{\partial\overline{\Psi}_\beta}{\partial\phi_\alpha}. \tag{82}$$

Now, the conceptual difficulty in applying mixture theory to gels is apparent. *There is a manifold of choices for the individual free energy that produces the same sum.* Each choice will lead eventually to a different expression for the stress.

It can be shown that, ultimately, the field equations that govern the motion of the gel are independent on the choice. However, if we insist on prescribing traction boundary conditions in terms of stresses beforehand, different choices will lead to different mathematical statements.This point deserves a further clarification. In continuum mechanics a loading environment is modeled by prescribing boundary conditions of traction. These conditions are translated in terms of stress through the Cauchy relation (see (8)), regardless what the constitutive prescription for the stress be. Once the constitutive equation for the free energy is provided, these conditions lead to a precise mathematical statement through a sequence of steps **free of ambiguity**. For a superposition of continua, however, there is ambiguity concerning the expression of the partial stresses because of the manifold of choices for the free energies of the individual components. As a result, the same set of boundary conditions of traction type, will lead to **different mathematical statements** concerning boundary conditions, according to what choice has been mad for the free energies.

## 10 The Duda Souza Fried model

The papers [7] and [6] adopt a different standpoint. The fluid-solid mixture is treated as a single homogenized continuum body which allows for a mass flux of the fluid.

$$\frac{\mathrm{d}}{\mathrm{d}t}\int \tag{83}$$

$$\frac{\mathrm{d}}{\mathrm{d}t} \tag{84}$$

An issue with the constitutive equations (**??**) is that chemical potential appears at the same time in the list of dependent and independent variables.

The free energy per unit referential volume of the solid constituent obeys the constitutive equation:

$$\Psi_s = \widetilde{\Psi}_s(\mathbf{F}, c),$$

where $c$ is the referential concentration of solvent (moles of fluid constituent per unit referential volume of the solid constituent). The incompressibility constraint $\det\mathbf{F} = 1 + vc$, where $v$ is the molar volume of the fluid. The fluid volume fraction

$\phi_f$ and the referential fluid concentration $c$ are related by

$$\phi_f = \frac{vc}{1+vc}.$$

Thus,

$$\widetilde{\Psi}_s(\mathbf{F}, c) = \widehat{\Psi}_s\left(\mathbf{F}, \frac{vc}{1+vc}\right)$$

The Piola stress tensor and the chemical potential in the DSF model are

$$\boldsymbol{S} = \frac{\partial \widehat{\Psi}_s}{\partial \mathbf{F}} - \lambda \mathbf{I},$$

and

$$\mu = \frac{\partial \widetilde{\Psi}_s}{\partial c} + \frac{v}{1+vc} q.$$

Thus, the Cauchy stress is

$$\mathbf{T} = \phi_s \frac{\partial \Psi_s}{\partial \mathbf{F}} \mathbf{F}^T - \phi_s \lambda \mathbf{I}$$

The chemical potential is given by

$$\mu = v \frac{\partial \Psi_s}{\partial \phi_f} \phi_s^2 + v \phi_s q.$$

I WOULD EXPECT THE CHEMICAL POTENTIAL TO BE GIVEN BY

$$\mu = v p_f$$

**Remark 13.** *The DSF model can be obtained from the Bowen model by taking $\psi = \psi_s$. This is equivalent, in the approach of Green and Naghdi, to choosing the fictitious velocity of the mixture to coincide with the velocity of the solid constituent.*

IS IS TRUE THAT THE DUAL STRESS OF THE VELOCITY OF THE MIXTURE IS THE SUM OF THE PARTIAL STRESSES?

# 11 Convection of free energy

Within the framework of mixture theories, one must pick, for each constituent $\alpha$, a constitutive prescription

$$\psi_\alpha = \widehat{\psi}_\alpha(\mathbf{F}_s, \phi_s, \phi_f)$$

delivering the spatial free energy density of that constituent. Yet, the system of partial differential equations generated by mixture theory depends only on the total spatial free energy density:

$$\psi = \sum_\alpha \psi_\alpha.$$

This, rather than being a coincidence, is a hint that from the energetic standpoint a mixture should be treated as a whole, and that deciding how to attribute a free energy to each constituent is a subtle choice that depends on the particular problem at hand.

Derivations of effective free energies for gels, in fact, generate only constitutive prescriptions for the total free energy density:

$$\widehat{\psi}(\mathbf{F}_s, \phi_s, \phi_f) = \phi_s \widehat{\sigma}(\mathbf{F}) + \widehat{\iota}(\phi_s, \phi_f),$$

where $\widehat{\sigma}(\mathbf{F})$ specifies constitutively is the referential strain energy $\sigma$ of the polymeric network and $\iota = \widehat{\iota}(\phi_s, \phi_f)$ is the interaction energy. Although physics suggests that one should think of the strain energy $\sigma$ as pertaining to the solid constituent, no physical argument can help us deciding how to split the interaction energy between the two constituents. The naive choice of splitting the interaction energy between the solid and fluid constituents according to their volume fractions leads to the constitutive prescription:

$$\psi_s = \phi_s(\sigma + \iota), \qquad \text{and} \qquad \psi_f = \phi_f \iota,$$

Yet, there seems to be no reason for preferring this choice to others, such as for example that proposed in [5].

Be it as it may, even if the motion equation generated from the theory do not depend on how one splits the free energy among the individual constituent, still the issue remains concerning the assignment of physically-sound boundary conditions. In fact, this issue, rather than being specific to gels, is more encompassing.

A possible remedy to this issue was devised by Green and Naghdi in [9]. Their approach to mixtures does not rely on the assignment of partial energies and entropies. The dissipation principle engendered by the theory of Green and Naghdi, when adapted to the present situation of an isothermal setting with incompressible constituents, takes the form:

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_{\Omega}\psi+\int_{\partial\Omega}\psi\mathbf{v}\cdot\mathbf{n}\leq\int_{\partial\Omega}\mathbf{T}_{\alpha}\cdot\operatorname{grad}\mathbf{v}_{\alpha}+\mathbf{f}_{\alpha}\cdot\mathbf{v}_{\alpha}, \qquad \text{eq:13} \tag{85}$$

where the velocity of the compound continuum

$$\mathbf{v}=\sum_{\alpha}\phi_{\alpha}\mathbf{v}_{\alpha} \qquad \text{eq:14} \tag{86}$$

is computed by weighting the individual velocities according to their volume fraction.

In my opinion, the formulation (87) is not a remedy to the issue that here is being raised. In fact, the dissipation inequality (87) is contingent on choosing the expression (86) for the representative velocity of the continuum, a choice that seems to be not compulsory. As a matter of fact, (87) can be recovered as a special case of Bowen's dissipation principle by defining the free energies of the individual components as $\psi_{\alpha}:=\phi_{\alpha}\psi$ (in other words, each component is ascribed a quota of free energy proportional to its volume fraction).

Our point of view is that one should not split the free energy among different constituents, and should replace the dissipation principle (87) with the weaker statement

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_{\Omega}\psi+\int_{\partial\Omega}\xi\leq\int_{\partial\Omega}\mathbf{T}_{\alpha}\cdot\operatorname{grad}\mathbf{v}_{\alpha}+\mathbf{f}_{\alpha}\cdot\mathbf{v}_{\alpha}, \qquad \text{eq:13} \tag{87}$$

where $\xi$ is a boundary flux to be specified constitutively. That the specification of $\xi$ must not be provided in advance is suggested by the fact that in the case of a single component the expression of $\xi$ can be derived from thermodynamics, as we illustrate in the next section.

# 12 Mixture of fluids: The expression of the convecting term as a consequence of the dissipation inequality

## 12.1 The standard case with single constituent

In the case of a single constituent, the spatial version of the dissipation inequality (87) reduces to the well–known form:

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_{\Omega}\psi+\int_{\partial\Omega}\psi\mathbf{v}\cdot\mathbf{n}\leq\int_{\partial\Omega}\mathbf{T}\cdot\operatorname{grad}\mathbf{v}. \qquad \text{eq:24} \tag{88}$$

The second integral on the left–hand side is the *convective term* associated to the influx of free energy in the *spatial control region* $\Omega$.

Let us recapitulate how, in the case of a single constituent, the dissipation inequality is used to deduce restrictions on the constitutive equations. To expedite the discussion we consider the case when the spatial free energy depends only on the specific volume $\phi$, that is, $\psi=\widehat{\psi}(\phi)$. We have

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\int_{\Omega}\psi= & -\int_{\Omega}\frac{\partial\psi}{\partial\phi}\operatorname{grad}\phi\cdot\mathbf{v}-\int_{\Omega}\frac{\partial\psi}{\partial\phi}\phi\operatorname{div}\mathbf{v}\\ & -\int_{\Omega}\operatorname{grad}\psi\cdot\mathbf{v}-\int_{\Omega}\frac{\partial\psi}{\partial\phi}\phi\operatorname{div}\mathbf{v}\\ = & -\int_{\partial\Omega}\psi\mathbf{v}\cdot\mathbf{n}-\int_{\Omega}\left(\frac{\partial\psi}{\partial\phi}\phi-\psi\right)\operatorname{div}\mathbf{v}.\end{aligned}$$

Thus, the dissipation inequality (88) reduces to

$$-\int_{\Omega}\left(\frac{\partial\psi}{\partial\phi}\phi-\psi\right)\operatorname{div}\mathbf{v}\leq\int_{\partial\Omega}\mathbf{T}\cdot\operatorname{grad}\mathbf{v}. \qquad \text{eq:5} \tag{89}$$

This allows us to conclude that the stress is given by a hydrostatic equilibrium part and a dissipative part: $\mathbf{T}=-p\mathbf{I}+\mathbf{T}^{(d)}$, with

$$p=\frac{\partial\psi}{\partial\phi}\phi-\psi$$

the *hosmotic pressure* and with the dissipative stress $\mathbf{T}^{(d)}$ satisfying the residual dissipation inequality: $\int_{\partial\Omega}\mathbf{T}^{(d)}\cdot\operatorname{grad}\mathbf{v}\geq 0$.

## 12.2 The free-energy flux as a constitutive choice: a single fluid.

We are now going to show that the form of the convective term appearing in boundary integral on the left–hand side of the inequality (88) is dictated by thermodynamics. To this effect, let us replace (88) with the weaker statement

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_\Omega \psi + \int_{\partial\Omega} \xi \leq \int_{\partial\Omega} \mathbf{T}\cdot \operatorname{grad}\mathbf{v}, \qquad \text{eq:25} \quad (90)$$

where the integrand $\xi$ is an unspecified flux at the boundary of the control region $\Omega$.

Now, the argument used to draw restrictions on $\mathbf{T}$ can be used to gain information on $\xi$. Specifically, one deduces

$$\xi = \psi\mathbf{v}\cdot\mathbf{n}. \qquad \text{eq:26} \quad (91)$$

In fact, if we replicate the manipulation leading to (89) we now get

$$-\int_\Omega \left(\frac{\partial\psi}{\partial\phi}\phi - \psi\right)\operatorname{div}\mathbf{v} + \int_{\partial\Omega}(\xi - \psi\mathbf{v}\cdot\mathbf{n}) \leq \int_{\partial\Omega}\mathbf{T}\cdot\operatorname{grad}\mathbf{v}. \qquad (92)$$

The usual Coleman–Noll argument leads to (91).

Incidentally, the identification (91) can be arrived at by exploiting translational invariance of the internal power. Such inveriance on the right–hand side of (90) entails that if the velocity field undergoes the transformation:

$$\mathbf{v}(\mathbf{x}) \mapsto \mathbf{v}(\mathbf{x}) + \mathbf{w},$$

then first term on the left–hand side of (90) transforms according to:

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_\Omega \psi \mapsto \frac{\mathrm{d}}{\mathrm{d}t}\int_\Omega \psi + \int_\Omega \operatorname{grad}\psi\cdot\mathbf{w} = \frac{\mathrm{d}}{\mathrm{d}t}\int_\Omega \psi + \int_{\partial\Omega}\psi\cdot\mathbf{w}\cdot\mathbf{n}.$$

## 12.3 The free-energy flux as a constitutive choice: a mixture of two incompressible fluids.

Consider now a mixture of two constituents ($n = 2$), with spatial free energy density $\psi(\phi_1, \phi_2)$, so that both are fluids. We write the dissipation inequality as:

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_\Omega \psi - \int_\Omega \lambda \sum_\alpha (\phi_\alpha \operatorname{div}\mathbf{v}_\alpha + \operatorname{grad}\phi_\alpha\cdot\mathbf{v}_\alpha) + \int_{\partial\Omega}\xi \leq \int_\Omega \left(\sum_\alpha \mathbf{T}_\alpha\cdot\operatorname{grad}\mathbf{v}_\alpha + \mathbf{f}_\alpha\cdot\mathbf{v}_\alpha\right). \qquad \text{eq:20} \quad (93)$$

We have

$$
\begin{aligned}
\frac{\mathrm{d}}{\mathrm{d}t}\int_\Omega \psi &= \int_\Omega \psi_{,\alpha}\phi'_\alpha \\
&= -\int_\Omega \left(\psi_{,\alpha}\phi_\alpha \operatorname{div}\mathbf{v}_\alpha + \psi_{,\alpha}\operatorname{grad}\phi_\alpha\cdot\mathbf{v}_\alpha\right)
\end{aligned}
$$

Note that here we cannot write $\psi_{,\alpha}\operatorname{grad}\phi_\alpha\cdot\mathbf{v}_\alpha = \operatorname{grad}\psi\cdot\mathbf{v}_\alpha$. However, we can continue the calculation as follows:

$$
\begin{aligned}
&= -\int_\Omega \left(\psi_{,\alpha}\phi_\alpha \operatorname{div}\mathbf{v}_\alpha + \psi_{,\alpha}\operatorname{grad}\phi_\alpha\cdot\mathbf{v}_1 + \psi_{,2}\operatorname{grad}\phi_2\cdot(\mathbf{v}_2-\mathbf{v}_1)\right) \\
&= -\int_\Omega \left(\psi_{,\alpha}\phi_\alpha \operatorname{div}\mathbf{v}_\alpha + \operatorname{grad}\psi\cdot\mathbf{v}_1 + \psi_{,2}\operatorname{grad}\phi_2\cdot(\mathbf{v}_2-\mathbf{v}_1)\right) \\
&= -\int_\Omega \left(\psi_{,1}\phi_1 \operatorname{div}\mathbf{v}_1 + \psi_{,2}\phi_2 \operatorname{div}\mathbf{v}_2 + \operatorname{grad}\psi\cdot\mathbf{v}_1 + \psi_{,2}\operatorname{grad}\phi_2\cdot(\mathbf{v}_2-\mathbf{v}_1)\right) \\
&= -\int_\Omega \left((\psi_{,1}\phi_1-\psi) \operatorname{div}\mathbf{v}_1 + \psi_{,2}\phi_2 \operatorname{div}\mathbf{v}_2 + \psi_{,2}\operatorname{grad}\phi_2\cdot(\mathbf{v}_2-\mathbf{v}_1)\right) - \int_{\partial\Omega}\psi\mathbf{v}_1\cdot\mathbf{n}.
\end{aligned}
$$

The same argument as in the previous section leads us to making the following identifications:

$$
\mathbf{T}_1 = (\psi - (\psi_{,1}+\lambda)\phi_1)\mathbf{I}, \qquad \mathbf{T}_2 = -(\psi_{,2}+\lambda)\phi_2\mathbf{I}, \qquad -\mathbf{f}_1 = \mathbf{f}_2 = \psi_{,2}\operatorname{grad}\phi_2,
$$

and

$$
\xi = \psi\mathbf{v}_1\cdot\mathbf{n}.
$$

In particular, the last equation shows that we are ascribing the entire free energy to the first constituent. Alongway the procedure leading to the previous constitutive identification, one may swap the two indices, thus obtaining a different condition for the stress.

# 13 Conclusions

The application of mixture theory to gels demands that the overall free energy be split between the individual components of the mixture. In a polymer gel, the free energy is the sum of a strain energy, stored in the stretched polymeric network, and a mixing energy, the latter being the sum of the entropic and enthalpic contributions that result upon mixing of the solid and the fluid.

While it is quite natural to ascribe the strain energy to the solid component, it is not clear how the mixing energy should be divided between the solid and the fluid, and one may wonder what are consequences of making one choice instead of another. Different choices are not equivalent from the modeling standpoint, since they determine different constitutive equations for the partial stresses of the mixture and for the interaction forces between its components. A more careful inspection shows, however, that when the constitutive equations are combined with the mechanical balance laws, the ensuing system of evolution equations is invariant with respect to the splitting of the free energy. Such invariance partly justifies the mixture-theoretic approach to gel modeling: whatever splitting of the mixing energy, such as for instance that proposed in [5], will yield the same system of evolution equations.

Be as it may, the interpretation of the energetic splitting required to apply mixture theory remains problematic. What is more, the fact that the resulting equations are eventually independent on the splitting is indeed a clue that energetic splitting could be in fact a superflous device, and that an attempt is worth towards a formulation of a theory of mixtures that relies on a single energy density.

This standpoind is in fact embraced in the works of Green and Naghdi [9, 10] who work with a single free energy for the mixture. However, when taking this standpoint, it seems unavoidable that the partwise free-energy imbalance be written in the Eulerian setting, using spatial rather than referential control volumes. When switching to the Eulerian setting one is expected to include in the free energy imbalance a convective term accounting for the outflow/inflow of free energy from/in the control volume (for otherwise frame indifference would be violated).

Invariably in all papers, the convective term is written as the integral over the boundary of the spatial free energy density multiplied by the projection along the outward normal of a gross velocity of the mixture. The choice of the gross velocity appears to be arbitrary: Green and Naghdi take the average of the velocities of the components weighted by their mass densities, while other workers take as weights the component volume fractions. Whatever the choice, the resulting dissipation principle is formally equivalent to splitting the free energy using the same weights adopted to define the gross velocity. Thus, one is again is to make a choice that appears arbitrary without additional physical clues.

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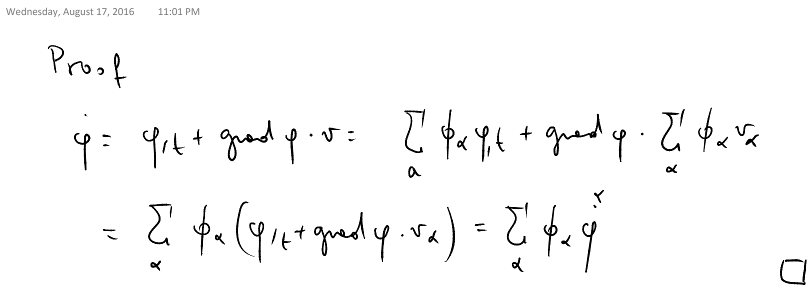
## Notes

1



Wednesday, August 17, 2016 11:01 PM

Proof

$$\dot{\varphi} = \varphi_{,t} + \operatorname{grad}\varphi \cdot v = \sum_{a}' \phi_\alpha \varphi_{,t} + \operatorname{grad}\varphi \cdot \sum_{\alpha}' \phi_\alpha v_\alpha$$

$$= \sum_{\alpha}' \phi_\alpha \left(\varphi_{,t} + \operatorname{grad}\varphi \cdot v_\alpha\right) = \sum_{\alpha}' \phi_\alpha \dot{\varphi}^{r}$$

□

*proof of Lemma 3.*

□

2

*Proof.* Proof of Prop. 3, new version, which I have checked

$$\sum_\alpha \grave{\psi}_\alpha = \sum_\alpha \frac{\partial \psi_\alpha}{\partial t} + \operatorname{grad}\psi_\alpha \cdot v_\alpha = \frac{\partial}{\partial t}\psi + \sum_\alpha \operatorname{grad}\psi_\alpha \cdot v_\alpha$$

$$= \frac{\partial\psi}{\partial F}\frac{\partial F_s}{\partial t} + \sum_\beta \frac{\partial\psi}{\partial\phi_\beta}\frac{\partial\phi_\beta}{\partial t} + \sum_\alpha \operatorname{grad}\psi_\alpha\cdot v_\alpha$$

$$= \frac{\partial\psi}{\partial F}\grave{F}_s - \frac{\partial\psi}{\partial F}\operatorname{grad}F\,[v_s]$$

$$+ \sum_\beta \frac{\partial\psi}{\partial\phi_\beta}\grave{\phi}_\beta - \frac{\partial\psi}{\partial\phi_\beta}\operatorname{grad}\phi_\beta\cdot v_\beta$$

$$+ \sum_\alpha \operatorname{grad}\psi_\alpha\cdot v_\alpha$$

$$\left( \grave{F}_s = \operatorname{grad} v_s\, F_s \qquad \grave{\phi}_\beta = -\phi_\beta \operatorname{div} v_\beta \right)$$

$$= \frac{\partial\psi}{\partial F} F_s^T\cdot \operatorname{grad} v_s - \sum_\beta \phi_\beta \frac{\partial\psi}{\partial\phi_\beta}\operatorname{div} v_\beta$$

$$+ \operatorname{grad}\psi_s\cdot v_s - \frac{\partial\psi}{\partial F}\cdot\operatorname{grad}F\,[v_s]$$

$$+ \sum_\beta \operatorname{grad}\psi_\beta\cdot v_\beta - \frac{\partial\psi}{\partial\phi_\beta}\operatorname{grad}\phi_\beta\cdot v_\beta$$

3

*Proof.* Proof of Prop. 3, oldest version, which I am not sure about

$$\sum_\alpha \phi_\alpha \overset{\circ}{\psi}_\alpha \quad \sum \overset{\circ}{\Psi}_\alpha - \dot{\phi}_\alpha \psi_\alpha$$

$$= \sum_\alpha \left[ \frac{\partial \Psi_\alpha}{\partial F_s} \cdot \overset{\alpha}{\dot{F}_s} + \left( \sum_{\beta \geq 2} \frac{\partial \Psi_\alpha}{\partial \phi_\beta} \overset{\alpha}{\dot{\phi}_\beta} \right) - \dot{\phi}_\alpha \psi_\alpha \right]$$

$$= \sum_\alpha \left[ \frac{\partial \psi_\alpha}{\partial F_s} \cdot \left( \dot{F}_s + \operatorname{grad} F_s \, (v_\alpha - v_s) \right) \right.$$

$$+ \sum_{\beta \geq 2} \frac{\partial \Psi_\alpha}{\partial \phi_\beta} \left( \underset{\overset{\shortparallel}{-\phi_\beta \, \mathrm{div} \, \underline{v}_\beta}}{\dot{\phi}_\beta} + \operatorname{grad} \phi_\beta \cdot (v_\alpha - v_\beta) \right)$$

$$\left. - \dot{\phi}_\alpha \psi_\alpha \right]$$

$$= \frac{\partial \Psi}{\partial F_s} F_s^T \cdot \dot{F}_s F_s^{-1} - \sum_{\beta \geq 2} \frac{\partial \Psi}{\partial \phi_\beta} \phi_\beta \, \mathrm{div} \, v_\beta$$

$$+ \sum_\alpha \left[ \frac{\partial \Psi_\alpha}{\partial F_s} \cdot \operatorname{grad} F_s \, (v_\alpha - v_s) + \sum_\beta \frac{\partial \Psi_\alpha}{\partial \phi_\beta} \operatorname{grad} \phi_\beta \, (v_\alpha - v_\beta) \right]$$

$$+ \sum_\alpha \phi_\alpha \psi_\alpha \, \mathrm{div} \, v_\alpha$$

$$= \left( \frac{\partial \Psi}{\partial F_s} F_s^T + \Psi_s I \right) \cdot \operatorname{grad} v_s - \sum_{\beta \geq 2} \left( \frac{\partial \Psi}{\partial \phi} \phi_\beta - \Psi_\beta \right) \mathrm{div} \, v_\beta$$

$$+ \sum_\alpha \left[ \frac{\partial \Psi_\alpha}{\partial F_s} \cdot \operatorname{grad} F_s \, (v_\alpha - v_s) + \sum_\beta \frac{\partial \Psi_\alpha}{\partial \phi_\beta} \operatorname{grad} \phi_\beta \, (v_\alpha - v_s) \right]$$

$$- \sum_\alpha \sum_\beta \frac{\partial \Psi_\alpha}{\partial \phi_\beta} \operatorname{grad} \phi_\beta \cdot (v_\beta - v_s)$$

$$= \left( \frac{\partial \underline{\Psi}}{\partial F_s} F_s^T + \underline{\Psi}_s I \right) \cdot \operatorname{grad} v_s - \sum_{\beta \geq 2} \left( \frac{\partial \underline{\Psi}}{\partial \phi} \phi_\beta - \underline{\Psi}_\beta \right) \operatorname{div} v_\beta$$

$$+ \sum_\alpha \operatorname{grad} \underline{\Psi}_\alpha \cdot (v_\alpha - v_s)$$

$$- \sum_\beta \frac{\partial \underline{\Psi}}{\partial \phi_\beta} \operatorname{grad} \phi_\beta \cdot (v_\beta - v_s)$$

$$= \left( \frac{\partial \underline{\Psi}}{\partial F_s} F_s^T + \underline{\Psi}_s I \right) \cdot \operatorname{grad} v_s - \sum_{\beta \geq 2} \left( \frac{\partial \underline{\Psi}}{\partial \phi} \phi_\beta - \underline{\Psi}_\beta \right) \operatorname{div} v_\beta$$

$$+ \sum_\alpha \left( \operatorname{grad} \underline{\Psi}_\alpha - \frac{\partial \underline{\Psi}}{\partial \phi_\alpha} \operatorname{grad} \phi_\alpha \right) \cdot (v_\alpha - v_s)$$

We thus have :

$$- \sum_\alpha{}' \phi_\alpha \dot{\psi}_\alpha + \sum_\alpha \left( T_\alpha - \lambda \phi_\alpha \right) \cdot \operatorname{grad} v_\alpha + \left( f_\alpha - \lambda \operatorname{grad} \phi_\alpha \right) \cdot v_\alpha$$

$$= - \sum_\alpha{}' \phi_\alpha \dot{\psi}_\alpha + \sum_\alpha \left( T_\alpha - \lambda \phi_\alpha \right) \cdot \operatorname{grad} v_\alpha + \left( f_\alpha - \lambda \operatorname{grad} \phi_\alpha \right) \cdot (v_\alpha - v_s)$$

$$\boxed{\sum f_\alpha = 0, \quad \sum \operatorname{grad} \phi_\alpha = 0}$$

$$= \left( T_s - (\lambda \phi_s + \underline{\Psi}_s) I - \frac{\partial \underline{\Psi}}{\partial F_s} F_s^T \right) \cdot \operatorname{grad} v_s$$

$$+ \sum_{\beta \geq 2} \left( T_\beta - (\lambda \phi_\beta + \underline{\Psi}_\beta) I + \frac{\partial \underline{\Psi}}{\partial \phi} \phi_\beta I \right) \cdot \operatorname{grad} v_\beta$$

$$+ \sum_\alpha \left( f_\alpha - \lambda \operatorname{grad} \phi_\alpha - \operatorname{grad} \underline{\Psi}_\alpha + \frac{\partial \underline{\Psi}}{\partial \phi_\alpha} \operatorname{grad} \phi_\alpha \right) \cdot (v_\alpha - v_s) \geq 0$$

$$= -\left(\phi_s K_s + \frac{\partial \Psi}{\partial F_s} F_s^T\right) \cdot \operatorname{grad} v_s$$

$$- \sum_{\beta \geq 2} \left( \phi_\beta K_\beta - \phi_\beta \frac{\partial \Psi}{\partial \phi_\beta} I \right) \cdot \operatorname{grad} v_\beta$$

$$+ \sum_{\beta \geq 2} \left( f_\beta - \lambda \operatorname{grad} \phi_\beta - \operatorname{grad} \Psi_\beta + \frac{\partial \Psi}{\partial \phi_\beta} \operatorname{grad} \phi_\beta \right) \cdot (v_\beta - v_s) \geq 0$$

$$=: -\phi_s K_s^{(d)} \cdot \operatorname{grad} v_s - \sum_{\beta \geq 2} \phi_\beta K_\beta^{(d)} \cdot \operatorname{grad} v_\beta$$

$$+ \sum_{\beta \geq 2} f_\beta^{(d)} \cdot (v_\beta - v_s) \geq 0$$