

Thermo-chemo-electro-mechanical formulation of saturated charged porous solids

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Thermo-Chemo-Electro-Mechanical Formulation of Saturated Charged Porous Solids

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Abstract. A thermo-chemo-electro-mechanical formulation of quasi-static finite deformation of swelling incompressible porous media is derived from a mixture theory including the volume fraction concept. The model consists of an electrically charged porous solid saturated with an ionic solution. Incompressible deformation is assumed. The mixture as a whole is assumed locally electroneutral. Different constituents following different kinematic paths are defined: solid, fluid, anions, cations and neutral solutes. Balance laws are derived for each constituent and for the mixture as a whole. A Lagrangian form of the second law of thermodynamics for incompressible porous media is used to derive the constitutive restrictions of the medium. The material properties are shown to be contained in one strain energy function and a matrix of frictional tensors. A principle of reversibility results from the constitutive restrictions. Existing theories of swelling media should be evaluated with respect to this principle.

Key words: mixture theory, biology, hydrogel, shale, polymer.

Nomenclature

a, A	scalar.
\mathbf{a}	vector.
\mathbf{A}	tensor
\mathbf{a}	column.
$\underline{\mathbf{A}}$	matrix.
\mathbf{b}^α	body force of constituent α per unit volume constituent.
\mathbf{b}	body force of the mixture per unit mixture volume.
$\mathbf{B}^{\beta\gamma}$	frictional tensor between constituents β and γ .
C^α	concentration of constituent α per unit current mixture volume.
\mathbf{E}	Green strain tensor of the solid.
F	Faraday's constant.
\mathbf{F}	deformation gradient tensor of the solid.
J	ratio of current mixture volume over initial mixture volume.
n^α	ratio of current volume of constituent α over current mixture volume.
N^α	ratio of current volume of constituent α over initial mixture volume.
p	pressure.
\mathbf{q}^α	heat flux of constituent α .
\mathbf{q}	an energy flux of the mixture (23).
r^α	heat supply of constituent α per unit volume constituent.
r	heat supply of the mixture per unit mixture volume.

\mathbf{v}^α	velocity of constituent α .
$\mathbf{v}^{\alpha s}$	Lagrangian velocity of constituent α relative to the solid.
\mathbf{v}^{qs}	Lagrangian form of energy flux \mathbf{q} .
\bar{V}^α	molar volume of constituent α .
W	Helmholtz free energy per unit initial mixture volume.
z^α	valence of constituent α .
ϵ^α	internal energy of constituent α per unit volume constituent.
ϵ	internal energy of the mixture per unit volume.
η^α	entropy of constituent α per unit volume constituent.
η	entropy of the mixture per unit volume.
η_0	entropy of the mixture per unit initial mixture volume.
μ^α	electrochemical potential of constituent α per unit volume constituent.
π^α	momentum interaction of constituent α .
Ψ^α	Helmholtz free energy of constituent α per unit volume constituent.
ψ^α	Helmholtz free energy of constituent α per unit mixture volume.
σ^α	partial Cauchy stress of constituent α .
θ^α	temperature of constituent α .
θ	temperature of the mixture.
∇	gradient operator in current configuration.
∇_0	gradient tensor in initial configuration.

1. Introduction

Many biological, mineral and synthetic porous media exhibit swelling or shrinking when in contact with changing salt concentrations. This phenomenon, observed in clays, shales, cartilage and gels, is caused by electric charges fixed to the solid, counteracted by corresponding charges in the fluid. These charges result in a variety of features, including swelling, electro-osmosis, streaming potentials and streaming currents. In physiology, quantitative understanding of both intracellular and extracellular events requires correct modelling of these phenomena in deforming tissue. At least four components are involved in the swelling mechanics: a solid; a fluid; anions; and cations. Lai *et al.* [7] have realized a major breakthrough by developing a triphasic theory for soft hydrated tissue. The three phases involved are the solid, the fluid and the ionic phase. They have applied the theory to cartilage while neglecting geometric nonlinearities. They have verified the theory for one-dimensional equilibrium results of swelling. Sherwood [8], working in the field of petroleum engineering, has presented a triphasic model of shale poroelasticity which, unlike the theory of Lai *et al.* does not include electrical charges. Snijders *et al.* [10] have developed a family of finite elements for two-dimensional, three-dimensional and axisymmetric analysis of finite deformation of triphasic media. This novel finite element software features fixed charge density as one of its inputs. However, they use it only to model Donnan osmotic swelling and ignore both electrical current and electric potential fields within the medium. Oomens *et al.* [14] have performed swelling pressure experiments and confined swelling and compression experiments on an acrylamide acrylic acid copolymer gel and have found the gel properties analogous to properties of soft charged hydrated tissue as measured by Drost *et al.* [13]. The model of Snijders

Table I. Direct and coupled flow phenomena in charged porous media

Flow/force	Pressure	Chemical potential	Electric potential	Temperature
Fluid	filtration	osmosis	electro-osmosis	thermo-osmosis
Solute	ultrafiltration	diffusion	electroforesis	thermal diffusion
Current	streaming current	diffusion current	electric conduction	thermo-electricity
Heat	isothermal heat transfer	Dufour effect	Peltier effect	thermal conduction

et al. has been unable to fit the experimental data of either of the two materials. Huyghe and Janssen [23] have developed a finite deformation quadriphasic theory which includes both electric current and electric potential, and which has turned out to fit experimental data of confined swelling and compression reasonably well, using material parameters consistent with other experimental data [24].

The key role of swelling in the behaviour of shales [17] and the associated problems of bore hole instability in shale drilling force petroleum engineers to develop continuum models of swelling shales. Numerous difficulties are associated with *in situ* measurement of relevant quantities around the borehole and with taking adequate samples of shale for subsequent testing in the laboratory. Therefore, there is a need for advanced models able to translate the experimental data available into predictions of the *in situ* situation. Unlike biological tissues, the shale is exposed to high overburden loads – in the order of hundreds of atmospheres – causing swelling forces other than osmosis to play a dominant role. Heidug and Wong [15] have developed a triphasic model which includes hydration forces in addition to osmosis, and have applied it to shales.

Table I gives an overview of direct and coupled flow phenomena induced by pressure, chemical potential, electrical potential and temperature gradients in charged porous media [16].

In this paper, we present a theory of swelling incompressible charged porous media. In order to simplify the mathematics as much as possible, a Lagrangian form of the entropy inequality [18] is used which leads to equations consistent with Biot's porous media theories in a more straightforward way than the more familiar Eulerian approach of Bowen [5]. The saturation and electroneutrality conditions are introduced by means of two Lagrange multipliers; the latter is physically interpreted as an electrical potential, the former as a pressure.

2. Theory

We assume all constituents α intrinsically incompressible, that is if one adds a mass m of constituent α to the mixture, the added volume of the mixture is always proportional to the mass m , irrespective of the value m , of the initial composition of

the mixture or of the state of deformation. The proportionality constant, the intrinsic density

$$\rho_i^\alpha = \frac{\rho^\alpha}{n^\alpha}, \quad (1)$$

is constant. ρ^α represents the apparent density of the α th constituent. n^α is the volume fraction of the α th constituent. We use the word incompressible in the sense used by Bowen [5]: deformation of the constituents does not result in changes of intrinsic densities, nor do changes in mixing ratios result in changes of intrinsic densities. Although it is more common to express solute quantities in molar or mass values than in volume values, we will use volume fractions throughout this paper, to reduce the number of symbols introduced. Because of incompressibility, the ratio between mass and volume is constant, and the two quantities are interchangeable in the equations. Excluding mass transfer between constituents, the mass balance of each constituent is then written as

$$\frac{\partial n^\alpha}{\partial t} + \nabla \cdot (n^\alpha \mathbf{v}^\alpha) = 0, \quad (2)$$

in which \mathbf{v}^α is the velocity of constituent α and ∇ the Eulerian gradient operator. As we assume saturation, we find

$$\sum_{\alpha} n^\alpha = 1. \quad (3)$$

We will agree that summation over α is taken over all constituents and summation over β or γ is taken over all constituents but the solid. Differentiation of Equation (3) with respect to t and substitution of the mass balance equations (2) yields the mass balance of the mixture

$$\nabla \cdot \mathbf{v}^s + \sum_{\beta} \nabla \cdot [n^\beta (\mathbf{v}^\beta - \mathbf{v}^s)] = 0. \quad (4)$$

The deformation gradient tensor \mathbf{F} maps an infinitesimal material line segment in the initial state of the solid onto the corresponding line segment in the current state. The relative volume change from the initial to the current state is the determinant of the deformation gradient tensor $J = \det \mathbf{F}$. If we introduce volume fractions

$$N^\alpha = J n^\alpha \quad (5)$$

per unit initial volume, we can rewrite the mass balance equation (2) as follows:

$$\frac{D^s N^\alpha}{Dt} + J \nabla \cdot [n^\alpha (\mathbf{v}^\alpha - \mathbf{v}^s)] = 0 \quad (6)$$

when using the identity

$$\frac{D^s J}{Dt} = J \nabla \cdot \mathbf{v}^s. \quad (7)$$

In Equations (6) and (7), $D^s/Dt = \partial/\partial t + \mathbf{v}^s \cdot \nabla$ is the time derivative for an observer moving with the solid. The electrostatic interactions between ions and the charged solid are accounted for by means of an electroneutrality condition. Disturbances of charge neutrality are corrected in such media in a time lapse in the order of the quotient of the dielectric constant over the electrical conductivity of the medium. The order of magnitude of this time constant is 1 ns [11]. As we are not concerned with phenomena faster than 1 μ s, we assume electroneutrality to be valid at all times. Magnetic fields generated by the electric fluxes through the medium are considered negligible. The electroneutrality condition requires that

$$C^{fc} + \sum_{\beta} z^{\beta} C^{\beta} = 0, \quad (8)$$

in which z^{β} are the valences, C^{fc} the fixed charge density per unit initial mixture volume and C^{β} the current molar concentration of mobile ions in the solvent per unit initial mixture volume

$$C^{\beta} = \frac{N^{\beta}}{\bar{V}^{\beta}}, \quad (9)$$

in which \bar{V}^{β} are the partial molar volumes of the solvent and solutes. Equation (8) is rewritten in a more convenient differentiated form, using the fixity of the fixed charges ($D^s C^{fc}/Dt = 0$) and Equation (9) [23]

$$\sum_{\beta} \frac{z^{\beta}}{\bar{V}^{\beta}} \nabla \cdot [n^{\beta}(\mathbf{v}^{\beta} - \mathbf{v}^s)] = 0. \quad (10)$$

Neglecting inertia, the momentum balance takes the form

$$\nabla \cdot (\boldsymbol{\sigma}^{\alpha})^C + \boldsymbol{\pi}^{\alpha} = n^{\alpha} \mathbf{b}^{\alpha}, \quad (11)$$

which, after summation over all constituents, yields

$$\nabla \cdot (\boldsymbol{\sigma})^C = \sum_{\alpha} \nabla \cdot (\boldsymbol{\sigma}^{\alpha})^C = \mathbf{b}, \quad (12)$$

if use is made of the balance condition:

$$\sum_{\alpha} \boldsymbol{\pi}^{\alpha} = \mathbf{0}, \quad (13)$$

$\boldsymbol{\sigma}^{\alpha}$ is the partial Cauchy stress tensor of constituent α , $\boldsymbol{\pi}^{\alpha}$ the momentum interaction with constituents other than α , \mathbf{b}^{α} the body force of constituent α per unit volume and $\mathbf{b} = \sum_{\alpha} n^{\alpha} \mathbf{b}^{\alpha}$ the body force of the mixture per unit volume. The partial Cauchy stress is defined for all constituents in the same way in accordance with standard literature, for example [12]. One should expect, for example, that electrostatic interactions cause significant forces between mobile ions. Balance of

moment of momentum requires that the stress tensor $\boldsymbol{\sigma}$ be symmetric. If no moment of momentum interaction between components occurs, the partial stresses $\boldsymbol{\sigma}^\alpha$ are also symmetric. In this paper we assume all partial stresses to be symmetric. The balance of energy for the α th constituent reads

$$n^\alpha \frac{D^\alpha \epsilon^\alpha}{Dt} = \boldsymbol{\sigma}^\alpha : \nabla \mathbf{v}^\alpha - \nabla \cdot \mathbf{q}^\alpha + n^\alpha r^\alpha + \hat{\epsilon}^\alpha, \quad (14)$$

in which ϵ^α is the partial internal energy of the α th constituent per unit volume, \mathbf{q}^α the heat flux of constituent α , r^α the partial heat supply per unit volume constituent and $\hat{\epsilon}^\alpha$ the energy interaction with other constituents per unit volume. Total energy balance requires

$$\sum_\alpha (\hat{\epsilon}^\alpha + \mathbf{v}^\alpha \cdot \boldsymbol{\pi}^\alpha) = 0. \quad (15)$$

Substitution of Equation (14) into Equation (15) yields an equivalent form of the total energy balance

$$\frac{D^s \epsilon}{Dt} = \sum_\alpha \{ \boldsymbol{\sigma}^\alpha : \nabla \mathbf{v}^\alpha - \nabla \cdot [\mathbf{q}^\alpha + n^\alpha \epsilon^\alpha (\mathbf{v}^\alpha - \mathbf{v}^s)] - \mathbf{v}^\alpha \cdot \boldsymbol{\pi}^\alpha \} - \epsilon \nabla \cdot \mathbf{v}^s + r, \quad (16)$$

in which

$$\epsilon = \sum_\alpha n^\alpha \epsilon^\alpha \quad (17)$$

is the internal energy of the mixture per unit volume and

$$r = \sum_\alpha n^\alpha r^\alpha \quad (18)$$

is the total heat supply of the mixture per unit volume. Under incompressible conditions, the entropy inequality for a unit volume of mixture reads [5]

$$\frac{D^s \eta}{Dt} - \eta \nabla \cdot \mathbf{v}^s + \sum_\alpha \left[\nabla \cdot \left(\frac{\mathbf{q}^\alpha}{\theta^\alpha} + n^\alpha \eta^\alpha (\mathbf{v}^\alpha - \mathbf{v}^s) \right) - \frac{n^\alpha r^\alpha}{\theta^\alpha} \right] \geq 0, \quad (19)$$

in which η^α is the entropy of constituent α per unit volume constituent, $\eta = \sum_\alpha n^\alpha \eta^\alpha$ is the entropy of the mixture per unit mixture volume and θ^α the temperature of the constituent α . If the temperature field is assumed to be the same for all constituents, we find

$$\frac{D^s \eta}{Dt} - \eta \nabla \cdot \mathbf{v}^s + \nabla \cdot \left[\frac{1}{\theta} \sum_\alpha (\mathbf{q}^\alpha + n^\alpha \eta^\alpha \theta (\mathbf{v}^\alpha - \mathbf{v}^s)) \right] - \frac{r}{\theta} \geq 0, \quad (20)$$

in which θ is the temperature of the mixture. Substitution of the energy balance (16) into the entropy inequality eliminates the heat supply r from the inequality

$$-\eta \frac{D^s \theta}{Dt} - \frac{\mathbf{q} \cdot \nabla \theta}{\theta} + \sum_{\alpha} \left(-n^{\alpha} \frac{D^{\alpha} \Psi^{\alpha}}{Dt} + \boldsymbol{\sigma}^{\alpha} : \nabla \cdot \mathbf{v}^{\alpha} - \boldsymbol{\pi}^{\alpha} \cdot \mathbf{v}^{\alpha} \right) \geq 0, \quad (21)$$

in which

$$\Psi^{\alpha} = \epsilon^{\alpha} - \theta \eta^{\alpha} \quad (22)$$

is the Helmholtz free energy of constituent α per unit volume constituent and

$$\mathbf{q} = \sum_{\alpha} [\mathbf{q}^{\alpha} + n^{\alpha} \eta^{\alpha} \theta (\mathbf{v}^{\alpha} - \mathbf{v}^s)] \quad (23)$$

is an energy flux vector of the mixture. We introduce the strain energy function

$$W = J \sum_{\alpha} n^{\alpha} \Psi^{\alpha} = J \sum_{\alpha} \psi^{\alpha} \quad (24)$$

as the Helmholtz free energy of a mixture volume which in the *initial* state of the solid equals unity. ψ^{α} is the Helmholtz free energy of constituent α per unit mixture volume. Rewriting the inequality (21) for the entropy production per initial mixture volume – that is, we multiply inequality (21) by the relative volume change J – we find

$$\begin{aligned} & -J \eta \frac{D^s \theta}{Dt} - J \frac{\mathbf{q} \cdot \nabla \theta}{\theta} - \frac{D^s W}{Dt} + J \boldsymbol{\sigma} : \nabla \mathbf{v}^s - J \nabla \cdot \sum_{\beta} (\mathbf{v}^{\beta} - \mathbf{v}^s) \psi^{\beta} + \\ & + J \sum_{\beta} [\nabla (\mathbf{v}^{\beta} - \mathbf{v}^s) : \boldsymbol{\sigma}^{\beta} - (\mathbf{v}^{\beta} - \mathbf{v}^s) \cdot \boldsymbol{\pi}^{\beta}] \geq 0. \end{aligned} \quad (25)$$

The entropy inequality should hold for an arbitrary state of the mixture, complying with the balance laws, incompressibility, saturation and electroneutrality. There are two ways to comply with these restrictions. One is substitution of the restriction into the inequality, resulting in the elimination of a field variable. The other is by introduction of a Lagrange multiplier. The balance laws and the incompressibility conditions (1) are accounted for by means of substitution. The differentiated forms of the saturation condition (4) and the electroneutrality (10) are accounted for by means of a Lagrange multiplier. The inequality (25) shows that the apparent densities ρ^{α} , the body forces \mathbf{b}^{α} and the heat supplies r^{α} are already eliminated from the inequality. In other words the conditions of incompressibility (1) are fulfilled by choosing $\rho^{\alpha} = \rho_i^{\alpha} n^{\alpha}$, the momentum balances (11) are fulfilled by choosing \mathbf{b}^{α} accordingly and the energy balance is fulfilled by choosing the heat supply r accordingly. Therefore, restrictions still to be fulfilled are the mass balances, saturation and the electroneutrality. The differentiated form of the saturation condition (4) is

substituted by means of a Lagrange multiplier p

$$\begin{aligned}
& -\eta_0 \frac{D^s \theta}{Dt} - \frac{J \mathbf{v}^{qs} \cdot \nabla_0 \theta}{\theta} - \frac{D^s}{Dt} W + J \boldsymbol{\sigma}^{\text{eff}} : \nabla \mathbf{v}^s + \\
& + J \sum_{\beta} [\boldsymbol{\sigma}^{\beta} + (pn^{\beta} - \psi^{\beta}) \mathbf{I}] : \nabla (\mathbf{v}^{\beta} - \mathbf{v}^s) + \\
& + J \sum_{\beta} (\mathbf{v}^{\beta} - \mathbf{v}^s) \cdot (-\nabla \psi^{\beta} + p \nabla n^{\beta} - \boldsymbol{\pi}^{\beta}) \geq 0, \tag{26}
\end{aligned}$$

in which the effective stress $\boldsymbol{\sigma}^{\text{eff}}$ is defined as

$$\boldsymbol{\sigma}^{\text{eff}} = \boldsymbol{\sigma} + p \mathbf{I}, \tag{27}$$

the heat flux \mathbf{v}^{qs} through an area equal to unity in the initial state of the solid as

$$\mathbf{v}^{qs} = \mathbf{F}^{-1} \cdot \mathbf{q} \tag{28}$$

and the entropy per unit initial volume as

$$\eta_0 = J \eta. \tag{29}$$

Introducing the restriction (10) into inequality (26) by means of a Lagrange multiplier λ , yields

$$\begin{aligned}
& -\eta_0 \frac{D^s \theta}{Dt} - \frac{J \mathbf{v}^{qs} \cdot \nabla_0 \theta}{\theta} - \frac{D^s}{Dt} W + J \boldsymbol{\sigma}^{\text{eff}} : \nabla \mathbf{v}^s + \\
& + J \sum_{\beta} \left[\boldsymbol{\sigma}^{\beta} + \left(\left(p + \frac{z^{\beta} \lambda}{V^{\beta}} \right) n^{\beta} - \psi^{\beta} \right) \mathbf{I} \right] : \nabla (\mathbf{v}^{\beta} - \mathbf{v}^s) + \\
& + J \sum_{\beta} (\mathbf{v}^{\beta} - \mathbf{v}^s) \cdot \left[-\nabla \psi^{\beta} + \left(p + \frac{z^{\beta} \lambda}{V^{\beta}} \right) \nabla n^{\beta} - \boldsymbol{\pi}^{\beta} \right] \geq 0, \tag{30}
\end{aligned}$$

in which $\nabla_0 = \mathbf{F}^C \cdot \nabla$ is the gradient operator with respect to the initial configuration. We choose as independent variables the Green strain \mathbf{E} , the temperature θ , the Lagrangian form of the volume fractions of the fluid and the ions N^{β} , and of the relative velocities $\mathbf{v}^{\beta s} = \mathbf{F}^{-1} \cdot (\mathbf{v}^{\beta} - \mathbf{v}^s)$ and \mathbf{v}^{qs} . The dependent variables are the Helmholtz free energy per unit initial mixture volume W , the entropy per unit initial mixture volume η_0 , the effective stress $\boldsymbol{\sigma}^{\text{eff}}$ of the mixture, the Helmholtz free energy ψ^{γ} of constituent γ , the effective partial stresses $\boldsymbol{\sigma}^{\gamma} + (p + z^{\gamma} \lambda / \bar{V}^{\gamma}) n^{\gamma} \mathbf{I}$, the effective momentum interactions $\boldsymbol{\pi}^{\gamma} - (p + z^{\gamma} \lambda / \bar{V}^{\gamma}) \nabla n^{\gamma}$ and the temperature gradient $\nabla_0 \theta$. We apply the principle of equipresence, that is, all dependent variables depend on all independent variables, unless the entropy inequality requires otherwise:

$$W = W(\mathbf{E}, \theta, N^{\beta}, \mathbf{v}^{\beta s}, \mathbf{v}^{qs}), \tag{31}$$

$$\eta_0 = \eta_0(\mathbf{E}, \theta, N^{\beta}, \mathbf{v}^{\beta s}, \mathbf{v}^{qs}), \tag{32}$$

$$\boldsymbol{\sigma}^{\text{eff}} = \mathbf{F} \cdot \mathbf{S}^{\text{eff}}(\mathbf{E}, \theta, N^\beta, \mathbf{v}^{\beta s}, \mathbf{v}^{qs}) \cdot \mathbf{F}^C, \quad (33)$$

$$\psi^\gamma = \psi^\gamma(\mathbf{E}, \theta, N^\beta, \mathbf{v}^{\beta s}, \mathbf{v}^{qs}), \quad (34)$$

$$\boldsymbol{\sigma}^\gamma + \left(p + \frac{z^\gamma \lambda}{\bar{V}^\gamma} \right) n^\gamma \mathbf{I} = \mathbf{F} \cdot \mathbf{S}^\gamma(\mathbf{E}, \theta, N^\beta, \mathbf{v}^{\beta s}, \mathbf{v}^{qs}) \cdot \mathbf{F}^C, \quad (35)$$

$$\boldsymbol{\pi}^\gamma - \left(p + \frac{z^\gamma \lambda}{\bar{V}^\gamma} \right) \nabla n^\gamma = \mathbf{F} \cdot \mathbf{p}^\gamma(\mathbf{E}, \theta, N^\beta, \mathbf{v}^{\beta s}, \mathbf{v}^{qs}), \quad (36)$$

$$\nabla_0 \theta = \mathbf{g}_0(\mathbf{E}, \theta, N^\beta, \mathbf{v}^{\beta s}, \mathbf{v}^{qs}). \quad (37)$$

We apply the chain rule for time differentiation of W , which implies:

$$\begin{aligned} & - \left(\eta_0 + \frac{\partial W}{\partial \theta} \right) \frac{D^s \theta}{Dt} - \frac{\mathbf{v}^{qs} \cdot \nabla_0 \theta}{\theta} \left(J \boldsymbol{\sigma}^{\text{eff}} - \mathbf{F} \cdot \frac{\partial W}{\partial \mathbf{E}} \cdot \mathbf{F}^C \right) : \nabla \mathbf{v}^s - \\ & - \frac{\partial W}{\partial \mathbf{v}^{qs}} \cdot \frac{D^s \mathbf{v}^{qs}}{Dt} + \sum_\beta \left\{ - \frac{\partial W}{\partial \mathbf{v}^{\beta s}} \cdot \frac{D^s \mathbf{v}^{\beta s}}{Dt} + \right. \\ & + J[\boldsymbol{\sigma}^\beta + (\mu^\beta n^\beta - \psi^\beta) \mathbf{I}] : \nabla(\mathbf{v}^\beta - \mathbf{v}^s) + \\ & \left. + J(\mathbf{v}^\beta - \mathbf{v}^s) \cdot (-\nabla \psi^\beta + \mu^\beta \nabla n^\beta - \boldsymbol{\pi}^\beta) \right\} \geq 0, \end{aligned} \quad (38)$$

in which μ^β are the electrochemical potentials of constituents other than the porous solid

$$\mu^\beta = \frac{\partial W}{\partial N^\beta} + p + \frac{z^\beta \lambda}{\bar{V}^\beta}. \quad (39)$$

Comparison of the above equation to the classical equations of electrochemistry indicates that the Lagrange multiplier p can be interpreted as the fluid pressure and λ as the electrical potential of the medium multiplied by the constant of Faraday. Inequation (38) should be true for any value of the state variables. In view of the set of independent variables, the first term of (38) is linear in the time derivative of the temperature $D^s \theta / Dt$, the third term is linear in the solid velocity gradient $\nabla \mathbf{v}^s$, the fourth term linear in $(D^s / Dt) \mathbf{v}^{qs}$, the fifth term linear in $(D^s / Dt) \mathbf{v}^{\beta s}$ and the sixth term linear in the relative velocity gradients $\nabla(\mathbf{v}^\beta - \mathbf{v}^s)$. Therefore, by a standard argument [3], we find

$$\eta_0 = - \frac{\partial W}{\partial \theta}, \quad (40)$$

$$\boldsymbol{\sigma}^{\text{eff}} = \frac{1}{J} \mathbf{F} \cdot \frac{\partial W}{\partial \mathbf{E}} \cdot \mathbf{F}^C, \quad (41)$$

$$\frac{\partial W}{\partial \mathbf{v}^{qs}} = 0, \quad (42)$$

$$\frac{\partial W}{\partial \mathbf{v}^{\beta s}} = 0, \quad (43)$$

$$\boldsymbol{\sigma}^\beta = (\psi^\beta - \mu^\beta n^\beta) \mathbf{I}, \quad (44)$$

leaving as inequality

$$-\frac{J \mathbf{v}^{qs} \cdot \nabla_0 \theta}{\theta} + \sum_{\beta} J(\mathbf{v}^\beta - \mathbf{v}^s) \cdot (-\nabla \psi^\beta + \mu^\beta \nabla n^\beta - \boldsymbol{\pi}^\beta) \geq 0. \quad (45)$$

Equation (41) indicates that the effective stress of the mixture can be derived from a strain energy function W which represents the free energy of the mixture. Equation (43) shows that the strain energy function cannot depend on the relative velocities. Thus, the effective stress of a charged porous medium can be derived from a regular strain energy function, which physically has the same meaning as in single phase or biphasic media, but which can depend on both strain and solute concentrations in the medium. According to Equation (44), the partial stress of the fluid and the solutes are scalars. Transforming the relative velocities to their Lagrangian equivalents, we find, instead of (45),

$$-\frac{\mathbf{v}^{qs} \cdot \nabla_0 \theta}{\theta} + \sum_{\beta} \mathbf{v}^{\beta s} \cdot [-\nabla_0 \psi^\beta + \mu^\beta \nabla_0 n^\beta - \mathbf{F}^C \cdot \boldsymbol{\pi}^\beta] \geq 0. \quad (46)$$

If we assume that the system is not too far from equilibrium, we can express the dissipation (46) associated with relative flow of fluid, solutes and heat as a quadratic function of the relative velocities

$$-\nabla_0 \psi^\beta + \mu^\beta \nabla_0 n^\beta - \mathbf{F}^C \cdot \boldsymbol{\pi}^\beta = \sum_{\gamma} \mathbf{B}^{\beta\gamma} \cdot \mathbf{v}^{\gamma s} + \mathbf{B}^{\beta q} \cdot \mathbf{v}^{qs}, \quad (47)$$

$$-\frac{\nabla_0 \theta}{\theta} = \sum_{\gamma} \mathbf{B}^{q\gamma} \cdot \mathbf{v}^{\gamma s} + \mathbf{B}^{qq} \cdot \mathbf{v}^{qs}, \quad (48)$$

in which

$$\begin{bmatrix} \mathbf{B}^{\beta\gamma} & \mathbf{B}^{\beta q} \\ \mathbf{B}^{q\gamma} & \mathbf{B}^{qq} \end{bmatrix} \quad (49)$$

is a positive definite matrix of frictional tensors. Substituting Equations (11) and (44) into Equation (47) yields Lagrangian forms of the classical equations of irreversible thermodynamics

$$-n^\beta \nabla_0 \mu^\beta - \mathbf{F}^C \cdot n^\beta \mathbf{b}^\beta = \sum_{\gamma} \mathbf{B}^{\beta\gamma} \cdot \mathbf{v}^{\gamma s} + \mathbf{B}^{\beta q} \cdot \mathbf{v}^{qs}, \quad (50)$$

$$-\frac{\nabla_0 \theta}{\theta} = \sum_{\gamma} \mathbf{B}^{q\gamma} \cdot \mathbf{v}^{\gamma s} + \mathbf{B}^{qq} \cdot \mathbf{v}^{qs}. \quad (51)$$

The boundary conditions are given by a no-jump condition of the temperature, the electrochemical potential of the ions and the fluid across the boundary and the momentum balance of the boundary.

3. Discussion

The analysis presented in this paper differs in a few aspects from related work in the literature. We demonstrate that the constitutive behaviour needed for analysis of the deformation of swelling material (Equations (39)–(41), (50) and (51)) is entirely contained in the strain energy function W and the frictional matrix $\mathbf{B}^{\beta\gamma}$. This is a more compact description than the more classical Eulerian analysis requiring separate free energy functions to be evaluated for each constituent (e.g. [5, 7]) and might save a great deal of tedious work for experimentalists responsible for quantifying these constitutive functions. The definition of the function W as the Helmholtz free energy of a mixture volume equal to unity in the initial state of the solid is consistent with the classical definition of a strain energy function of a single phase material or of a saturated porous medium by Biot [4]. It is a straightforward extension of the work of Wilmansky on Lagrangian porous media models [20].

We apply the method of Coleman and Noll [3] to derive constitutive relationships from the second law of thermodynamics. This method has been criticized [21] and shown to be more restrictive than Mueller's method [19]. However, the criticisms are not shared by all experts in the field [19, 20], and for our purposes the use of either method is satisfactory.

Another feature distinguishes this thermodynamic analysis of swelling materials from the pioneering work of Lai *et al.* [7]. Lai *et al.* neglect to introduce the electroneutrality condition as a restriction on the second law of thermodynamics, although this condition mutually links the ion velocity gradients according to Equation (10). The electrical potential, obtained in our analysis as the Lagrange multiplier associated with the electroneutrality condition, is introduced in their analysis as an external volume force, which it is not. Our Lagrange multiplier λ is an internally generated electric field adding up to external electric fields contained in the body force vector \mathbf{b}^α .

Equations (39)–(41) are rewritten in their differentiated form

$$\begin{bmatrix} d\boldsymbol{\sigma}^{\text{eff}} \\ d\left(\mu^\beta - p - \frac{z^\beta\lambda}{V^\beta}\right) \\ -d\eta_0 \end{bmatrix} = \begin{bmatrix} \frac{\partial^2 W}{\partial \mathbf{E}^2} & \frac{\partial^2 W}{\partial N^\gamma \partial \mathbf{E}} & \frac{\partial^2 W}{\partial \theta \partial \mathbf{E}} \\ \frac{\partial^2 W}{\partial \mathbf{E} \partial N^\beta} & \frac{\partial^2 W}{\partial N^\gamma \partial N^\beta} & \frac{\partial^2 W}{\partial \theta \partial N^\beta} \\ \frac{\partial^2 W}{\partial \mathbf{E} \partial \theta} & \frac{\partial^2 W}{\partial N^\gamma \partial \theta} & \frac{\partial^2 W}{\partial \theta^2} \end{bmatrix} \begin{bmatrix} d\mathbf{E} \\ dN^\gamma \\ d\theta \end{bmatrix} \quad (52)$$

or

$$d\mathbf{y} = \underline{\mathbf{C}} d\mathbf{x}. \quad (53)$$

Assuming smoothness of the function W , the matrix $\underline{\mathbf{C}}$ should be symmetric. The existence of the function W and the symmetry of $\underline{\mathbf{C}}$ is closely associated with the principle of reversibility. This principle means that if the changes occur at an infinitely slow rate, the work done to bring the material from the initial condition to its final state

of strain and composition is independent of the path by which the final state is reached. In the absence of such a condition, an infinite amount of energy could be drawn from the material by loading and unloading it along a closed cycle. The above derivation generalises the approach of Huyghe and Janssen [23] to nonisothermal conditions in which temperatures are the same for all components. From the above equations several well-known physical theories can be derived [23], such as the Nernst equation for diffusion potentials, streaming potentials or the finite strain poroelasticity theory of Biot [4]. A field of application where temperature gradients may play an important role in swelling materials is for example human skin.

The reasons for choosing the quadriphasic theory [23] as a basis for the development are both experimental and conceptual. Alternative theories are available in the literature [7, 8, 10, 22]. Sherwood and Heidug have developed, triphasic theories in which fixed charges are absent altogether and, hence, in which electrical effects are not present. Although this is a valid approach for specific applications, it is not sufficient for our purposes, involving materials with high fixed charge densities. Snijders *et al.* [10] have handled somewhat less stringent assumptions. Lai *et al.* [7] have developed a triphasic theory in which fixed charges are included. Although at the outset the theory is general when applying it to articular cartilage, they assume that deformations are infinitesimal. Similar assumptions are handled by [22]. Gu *et al.* [9] have used the theory of Lai *et al.* in the context of one-dimensional permeation experiments. Those three papers use constitutive assumptions which lead to asymmetrical forms of the matrix $\mathbf{C}^{\beta\gamma}$. The chemical expansion stress \mathbf{T}_c as introduced by Lai *et al.* [7], for example, contributes to $\mathbf{C}^{s\beta}$, while corresponding lower-diagonal terms $\mathbf{C}^{\beta s}$ vanish. Although such an assumption is acceptable for infinitesimal theory, caution should be taken in extending such constitutive modelling to the finite strain domain. Moreover, recent comparison of experimental and numerical data on transient swelling [24] has not shown evidence of the existence of a chemical expansion stress.

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