Poromechanics of Compressible Charged Porous Media using the Theory of Mixtures

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Abstract:

Background. Osmotic, electro-static and/or hydrational swelling are essential mechanisms in the deformation behaviour of porous media, such as biological tissues, synthetic hydrogels and clay-rich rocks. Present theories are restricted to incompressible constituents.

Method of approach. An electro-chemo-mechanical formulation of quasi-static finite deformation of compressible charged porous media is derived from the theory of mixtures. The model consists of a compressible charged porous solid saturated with a compressible ionic solution. Four constituents following different kinematic paths are identified: a charged solid and three streaming constituents carrying either a positive, negative or no electrical charge, which are the cations, anions and fluid, respectively. The finite deformation model is reduced to infinitesimal theory.

Results. In the limiting case without ionic effects, the presented model is consistent with Biot's theory. Viscous drag compression is shown to be independent from the storage modulus.

Conclusions. Conflicts between poromechanics and mixture theory are only semantic in nature.

Keywords. Porous media, swelling, electro-osmosis, cartilage, bone, canaliculi, diffusion, shale., streaming potentials
I. Introduction

This paper focuses on the mechanics of swelling of biological, mineral and synthetic porous media. These materials exhibit swelling when in contact with changing salt concentrations. This swelling is caused by two factors: Donnan osmotic swelling and hydration or adsorption forces. Donnan osmosis is associated with electrical charges fixed to the solid, counteracted by corresponding charges in the fluid, which in turn attracts water, whereas, hydration results from the ordering of polar water molecules. As a consequence of the fixed charges a variety of physical phenomena are observed in these materials, such as streaming potentials, diffusion potentials, electro-osmosis, electro-phoresis [1].

**Biological materials**, consist mainly of water. A number of models for soft biological tissues have been developed in the past [2-4]. However, they all assume incompressibility of their constituents. Bone typically does not comply with this assumption. Bone is well known to exhibit streaming potentials under deformation. It is suspected that these streaming potentials are a key element in the understanding of bone mechanosensing and remodelling. [5].

**Synthetic hydrogels** also consist of large ionized molecules and are widely used in biomechanical research as a biomaterial e.g. as implants or tissue replacement, disposable medical devices and carriers of drugs [6]. An other promising application for these materials is to use them as an artificial material for reproducible experiments and verification of mathematical models [7]. Although in many applications,
constituents of hydrogel can be considered incompressible, under higher pressure this is not the case.

**Minerals** of the phyllosilicate class have a crystal structure consisting of silicate layers stacked upon each other [8], which becomes charged when exposed to water. In addition to the osmotic swelling on the macroscopic level, an electro-chemical interaction takes place inside the clay-mineral on a microscopic level and both, electrical repulsive forces due to the surface charge and hydration forces act as a swelling mechanism. The hydration forces, resulting from the ordering of polar water molecules, disjoin the stacked silicate layers [9]. Shale is a rock type containing a large amount of phyllosilicate type clay minerals. Swelling of shales is a major technical problem in petroleum engineering, which can severely threaten the stability of boreholes [10]. As down hole pressures are typically in the order of tens of MPa, compressibility of constituents is vital in these applications.

Several continuum approaches have been made towards developing constitutive models for porous media. Terzaghi [11] started the development of the idea of effective stress within the framework of the treatment of the consolidation problem for clay layers. Governing equations for a fluid-saturated poro-elastic solid have later been developed by Biot [12,13] and Biot and Willis [14], integrating the mechanical behaviour of porous solid and pore fluid with the transport of pore fluid. The pioneering work of Biot on porous media forms the basis for the research work in this field [15-20]. Biot [21] developed a finite deformation theory for porous solids, including physico-chemical effects. In this theory, the fluid pressure is replaced by a chemical potential for the capillary and adsorption effects. Heidug and Wong [22] developed shale swelling model, extending Biot's theory to incorporate an ionic phase in addition to the solid and the fluid. The hydration or adsorption force -in this theory- is dependent upon
the local ionic concentration, resulting in a swelling dependent upon salt concentration. Originally developed for gaseous and liquid chemical mixtures, the theory of mixtures has been shown to reproduce Biot's poromechanics theory. [23,24]. As compressibility and hydration are essential features in many problems of rock-mechanics and bone bio-mechanics particularly, the aim of this paper is to develop a model describing the swelling of a charged porous medium, with a compressible solid and fluid constituent, including the two swelling phenomena caused by, hydration forces and Donnan osmosis.

The model presented here uses the theory of porous media using the Lagrangian framework of Biot, which leads to equations consistent with Biot's porous media theory in a more straightforward way than the Eulerian approach [24]. Unlike in [24], the principle of equipresence is restrictly adhered to. In the limiting case without ionic and hydration effects, the resulting model is consistent with Biot's poro-elasticity theory.

II. Kinematics

The porous medium consists of an electrically charged porous solid matrix, saturated with an ionic solution. At any time \( t \) particles of the solid, fluid and ionic constituents occupy simultaneously the location \( x \):

\[
x = X_\alpha(X_\alpha, t), \ldots, \alpha = s, f, +, -.
\]

(1)

The subscript \( \alpha \) denotes the charged solid constituent (s), the fluid constituent (f) and the cations (+) and anions (−). \( X_\alpha \) is the initial position of constituent \( \alpha \) at time \( t \), and is generally different for each constituent. The fluid and ions are single species constituents, their molar volume \( V_\beta \) is defined as:
\[ \bar{V}_\beta = \frac{\partial V_\beta}{\partial N_\beta}, \ldots , \beta = f, +, - \]  

( \beta \text{ streaming constituents} ). \quad (2)

Herein, \( N_\beta \) denotes the number of mol of constituent \( \beta \) and index \( \beta \) denotes all the components other than the solid. The ionic constituents are assumed incompressible and equation (2) is written as:

\[ V_i = N_i \bar{V}_i, \ldots , i = +, - \]  

( \( i \) ionic constituents). \quad (3)

Where, \( V_i \) represents the volume added, by increasing \( N_i \) from zero to its present value.

Assuming the solid immiscible with the saturating ionic solution, the part of the mixture volume occupied by the volume of the solid \( V_s \), is physically distinguishable from the solution \((V_f + V_f + V_s)\). The mixture volume is defined as the sum of these partial volumes:

\[ V = V_s + \sum_{\beta=+,-} V_\beta. \quad (4) \]

The macroscopic quantities of the porous medium and of the constituents are defined at a scale, which is characterized by a length scale much greater than that of a pore but much less than that of the full system, e.g. the apparent density \( \gamma_a \) is defined as the volume integral of the partial mass over an averaging volume divided by the elementary volume:

\[ \gamma_a = \frac{M_a}{V}, \quad (5) \]

And the density of the porous medium reads:

\[ \gamma = \sum_{\alpha=s,f,+,-} \gamma_\alpha. \quad (6) \]

The volume fractions of the constituents \( n_\alpha \) are defined by:

\[ n_\alpha = \frac{V_\alpha}{V}. \quad (7) \]
Thus, $n_a$ represents the fraction of the mixture occupied by the $\alpha$th constituent.

Combination of the equations (4) and (7) yields the saturation condition:

$$n_s + n_l + n_r + n_\omega = 1 . \tag{8}$$

The 'true' or intrinsic density $\rho_a$ is defined as the volume integral of the partial mass over the averaging volume $M_\alpha$ divided by the partial or true volume:

$$\rho_a = \frac{M_\alpha}{V_\alpha} = \frac{n_a}{\gamma_a} . \tag{9}$$

The $\alpha$th constituent, occupying a position $X_\alpha$ at time $t = 0$, is carried to a new spatial position $x$ at time $t$ and this new position at time $t$ is given by the deformation function $\chi_a$ for the $\alpha$th constituent:

$$x = \chi_a (X_\alpha, t) . \tag{10}$$

Using the Lagrangian description of motion, the velocity field of $X_\alpha$ at time $t$ is defined by:

$$\frac{D}{Dt} (X_\alpha) = \frac{\partial \chi_a (X_\alpha, t)}{\partial t} , \tag{11}$$

herein, $D/Dt$ denotes the material time derivative for an observer following the motion of the $\alpha$th constituent (i.e. with fixed $X_\alpha$). In addition the deformation gradient is defined:

$$F_\alpha = (\nabla_0^a x_\alpha)^T , \tag{12}$$

where, $\nabla_0^a$ is the gradient operator with respect to the initial configuration of the $\alpha$th constituent:

$$\nabla_0^a = F_\alpha^T \cdot \nabla . \tag{13}$$

The velocity $v_s$ of the solid is defined as:
\[ \dot{x} = \frac{D^s}{Dt}(x) = v_s, \]  

(14)

herein, \( \dot{x} \) is the displacement of the solid component and the dot accent indicates the material time derivative 'following' the motion of the solid.

The Jacobian of the porous solid is:

\[ J = \left| \frac{dV_s}{dV_0} \right|, \]  

(15)

Differentiation with respect to time yields:

\[ \dot{J} = J \nabla \cdot v_s. \]  

(16)

The Green-Lagrange strain tensor for the porous skeleton is:

\[ \mathbf{E}_s = \frac{1}{2}(\mathbf{F}_s^T \cdot \mathbf{F}_s - \mathbf{I}). \]  

(17)

For all the non-solid or streaming constituents a description relative to the solid is used.

The velocity of the streaming constituents relative to the solid component \( v_{\beta} \) is defined as:

\[ v_{\beta s} = \frac{D^\beta}{Dt}(x) - v_s. \]  

(18)

A useful relation between \( D^\gamma /Dt \) and \( D^\beta /Dt \) is given by:

\[ \frac{D^\gamma}{Dt} = \frac{D^\beta}{Dt} - \nabla \cdot v_{\beta s}. \]  

(19)

in which, \( \psi(x,t) \) is any given scalar or vector field.

### III. Conservation and Constraint Equations

The mass balance equation for each component \( \alpha \) is expressed as:

\[ \frac{\partial \gamma_\alpha}{\partial t} + \nabla \cdot \gamma_\alpha v_\alpha = 0, \ldots \text{or} \ldots \frac{D^\alpha \gamma_\alpha}{Dt} + \gamma_\alpha \nabla v_\alpha = 0, \]  

(20)
In which $\frac{\partial}{\partial t}$ is the spatial time derivative. The balance of momentum equation for the $\alpha$th constituent is:

$$\gamma_a \frac{D^a v_a}{Dt} - \nabla \cdot \sigma_a^T - \gamma_a b_a = \hat{\pi}_a ,$$

with, $\sigma_a$ the partial stress tensor, $b_a$ the external body forces acting on the $\alpha$ constituent and $\hat{\pi}_a$ the momentum supplied by constituents other than $\alpha$. The principle of momentum conservation places the following restriction on the interaction terms:

$$\sum_{a=1,\ldots,n} \hat{\pi}_a = 0 .$$

The balance of moment of momentum equation for the $\alpha$th constituent is:

$$\sigma_a - \sigma_a^T = \hat{M}_a ,$$

with, $\hat{M}_a$ is the skew symmetric tensor corresponding to the axial vector representing the moment of momentum supplied by the other constituents. We assume there is no such moment of momentum interaction, resulting in symmetry of all partial stresses.

The balance of energy for the $\alpha$th constituent reads:

$$\gamma_a \left( \frac{D^a e_a}{Dt} - h_a \right) - \sigma_a : \nabla v_a + \nabla \cdot q_a + \hat{e}_a = \hat{\pi}_a ,$$

in which, $e_a$ is the partial internal energy, $q_a$ is the heat flux, $h_a$ is the partial heat and $\hat{e}_a$ is the energy interaction with other constituents.

The total energy balance requires:

$$\sum_{a=1,\ldots,n} (\hat{e}_a + \hat{\pi}_a \cdot v_a) = 0 .$$

The mixture balance equations (20) to (25) are recasted in a formulation relative to the solid. The inertial terms and body forces are neglected.
The mass balance equations of the streaming constituents (20) are rewritten in terms of the material time derivative 'following' the motion of the porous solid, using the equations (16) and (19):

\[ \dot{m}_s = 0, \quad \text{and} \quad \dot{m}_\beta + J \nabla \cdot (n_\beta \rho_\beta \mathbf{v}_\beta) = 0, \quad (26) \]

herein, the Lagrange apparent density \( m_\beta \) for the streaming constituents, represents the mass of constituent \( \beta \) currently contained in mixture volume that was initially equal to unity:

\[ m_\beta = J n_\beta \rho_\beta, \quad (27) \]

with, the superscript 0 referring to initial values.

Neglecting body forces and inertia, the momentum balance equation (21) takes the form:

\[ \nabla \cdot \mathbf{\sigma}_s = -\dot{\mathbf{p}}_s. \quad (28) \]

After summation over all the constituents this yields for the total stress tensor of the mixture:

\[ \nabla \cdot \mathbf{\sigma} = \sum_\alpha \nabla \cdot \mathbf{\sigma}_\alpha = 0. \quad (29) \]

The balance of energy for the solid constituent reads:

\[ n_\alpha \rho_\alpha (\dot{e}_s - h_s) - \mathbf{\sigma}_s : \nabla \mathbf{v}_s + \nabla \cdot \mathbf{q}_s = \dot{\mathbf{e}}_s, \quad (30) \]

and for the streaming constituents:

\[ n_\beta \rho_\beta (\dot{e}_\beta + \mathbf{v}_\beta : \nabla e_\beta - h_\beta) - \mathbf{\sigma}_\beta : \nabla \mathbf{v}_\beta + \nabla \cdot \mathbf{q}_\beta = \dot{\mathbf{e}}_\beta. \quad (31) \]

For each constituent the entropy equation is written as [25]:

\[ \gamma_\alpha \left( \frac{\partial x_\alpha}{\partial t} + \mathbf{\nabla} \cdot \frac{\mathbf{q}_\alpha}{\theta_\alpha} \right) = \mathbf{\xi}_\alpha, \quad (32) \]

in which, \( \eta_\alpha \) is the entropy density, \( \xi_\alpha \) is the entropy production and \( \theta_\alpha \) the partial temperature of the \( \alpha \)th constituent. Because the entropy production of a constituent may
be caused by entropy exchange with other constituents, the classical demand of a positive entropy production is not claimed for each individual constituent. Instead, the entropy production of the mixture as a whole must be positive or zero:

\[ \sum_{a=\text{d, r, c}} \xi_a \geq 0. \]  \hfill (33)

Next, the Helmholtz free energy, \( \Psi_a \), is defined:

\[ \Psi_a = (e_a - \theta_a \eta_a), \]  \hfill (34)

using the Helmholtz free energy the entropy inequality yields:

\[ \sum_{a=\text{d, r, c}} \gamma_a \left( -\frac{D^a \Psi_a}{Dt} + \frac{D^a e_a}{Dt} - \eta_a \frac{D^a \theta_a}{Dt} - h_a \right) + \nabla \cdot q_a \geq 0, \]  \hfill (35)

and this inequality should hold for an arbitrary state of the mixture.

As the fixed charges are fixed to the solid and disturbances of the space charge are corrected on a time scale associated with the diffusion of the electrical charges, which is much smaller than the time scale of fluid flow or ion diffusion [26], the porous medium has to obey the electro-neutrality constraint. By defining \( C^{\text{fc}} \) as the charge density fixed to the solid per unit initial mixture, the electro-neutrality restriction for the porous medium is:

\[ C^{\text{fc}} + \sum_{i=r, c} z_i C_i = 0, \]  \hfill (36)

herein, \( z_i \) are the valences and \( C_i \) the current molar concentrations of the ions per unit initial mixture. Differentiation of the electro-neutrality condition with respect to time and substitution into the mass balance equation of the ions yields the following electro-neutrality constraint:

\[ \sum_{i=r, c} z_i \frac{1}{V_i} J \nabla \cdot (\eta_i \Psi_a) = 0. \]  \hfill (37)
The constraint equation (44) is substituted into the entropy inequality by means of the Lagrange multiplier \( \lambda \). To facilitate the derivation of the constitutive laws the energy function \( W \) is introduced:

\[
W = J \sum_{\alpha=s,f,+,-} n_{\alpha} \rho_{\alpha} \psi_{\alpha} = J \sum_{\alpha=s,f,+,-} \psi_{\alpha},
\]

which, represents the Helmholtz free energy of the mixture per unit initial mixture volume. Rewriting the inequality (35) for the entropy production, using the strain energy function and assuming isothermal conditions yields:

\[
-\dot{W} + J \sigma : \nabla \mathbf{v} + J (\sigma_i - \psi_f I) : \nabla \mathbf{v}_s + J \sum_{i=r,-} [(\sigma_i + (\frac{\lambda z_i}{V_i}) n_i - \psi_i) I : \nabla \mathbf{v}_s]
\]

\[
+ J \mathbf{v}_s \cdot (-\mathbf{\hat{r}}_i - \nabla \psi_i) + J \sum_{i=r,-} [\mathbf{v}_s \cdot (-\mathbf{\hat{r}}_i + (\frac{\lambda z_i}{V_i}) \nabla n_i - \nabla \psi_i)] \geq 0
\]

**IV. Constitution**

The theory of constitution is dictated by the choice of independent variables. The axiom of equipresence of independent variables states that, all dependent variables must depend on all independent variables, except when the second law of thermodynamics requires otherwise. By means of the extended entropy inequality (39), restrictions are found for the dependent variables for the total mixture:

\[
\{W, \sigma\}
\]

and for the streaming constituents (\( \beta = f, +, - \)):

\[
\{\psi_{\beta}, \sigma_{\beta} + \frac{z_{\beta}}{V_{\beta}} \lambda n_{\beta} I, \mathbf{\hat{r}}_{\beta} - \frac{z_{\beta}}{V_{\beta}} \lambda \nabla n_{\beta}\}
\]

The dependent variables may be functions of a list of primary unknowns and a practical set based on experience and experimental work is chosen. The independent variables are:
{E_s, u_{βs}, ζ_β} .

Omission of the variables \( \dot{ρ}_c \) as dependent constitutive variables in the group of thermodynamic fluxes, excludes rate-dependent materials [27]. For the satisfaction of material-frame indifference the strain tensor \( E_s \) is used, instead of the displacement gradient tensor \( F_s \). To satisfy this same principle, the Lagrangian form of the relative velocities \( u_{βs} \) of the streaming constituents is used:

\[ u_{βs} = F_s^{-1} \cdot v_{βs} . \] (43)

Using the Biot terminology, the 'change in constituent content', \( ζ_β \) is adopted here in the list of independent variables, defined as:

\[ ζ_β = \frac{m_β}{ρ_β} . \] (44)

The principle of determinism states that constitutive equations must be formulated for the set of dependent variables (40) and (41), which are frame indifferent functions of the independent variables (42). For the mixture as a whole, these functions read:

\[ W = W(E_s, u_{βs}, ζ_β) , \]

\[ σ = F_s \cdot T(E_s, u_{βs}, ζ_β) \cdot F^c_s , \] (45)

and for the fluid this yields:

\[ Ψ_f = Ψ_f(E_s, u_{βs}, ζ_β) , \]

\[ σ_f = F_s \cdot S_f(E_s, u_{βs}, ζ_β) \cdot F^c_s , \]

\[ \hat{π}_f = F_s \cdot p_f(E_s, u_{βs}, ζ_β) , \] (46)

and for the ions this yields:

\[ Ψ_i = Ψ_i(E_s, u_{βs}, ζ_β) , \]

\[ σ_i + \frac{z_i}{V_i} λn_i I = F_s \cdot S_i(E_s, u_{βs}, ζ_β) \cdot F^c_s , \]

\[ \hat{π}_i - \frac{z_i}{V_i} λ∇n_i = F_s \cdot p_i(E_s, u_{βs}, ζ_β) . \] (47)
Applying the chain rule for time differentiation of strain energy function $W$ yields:

$$
\dot{W} = \frac{\partial W}{\partial \mathbf{E}_s} : \dot{\mathbf{E}}_s + \sum_{\beta=1,+,0} \left[ \frac{\partial W}{\partial \mathbf{u}_{\beta s}} \cdot \dot{\mathbf{u}}_{\beta s} + \frac{\partial W}{\partial \dot{\zeta}} \cdot \dot{\zeta}_\beta \right].
$$

Substituting (48) into the extended entropy inequality (39), yields for the inequality:

$$
J[\sigma - \frac{1}{J} \mathbf{F}_c - \frac{\partial W}{\partial \mathbf{F}_c}] : \nabla \mathbf{v}_s,
$$

$$
+ J \sum_{\beta=1,+,0} \left[ \left( \sigma_\beta + \left( \frac{n_\beta \rho_\beta}{\rho_\beta^0} \mu_\beta^e - \psi_\beta \right) \mathbf{1} \right) : \nabla \mathbf{v}_{\beta s} \right] -
\sum_{\beta=1,+,0} \left[ \frac{\partial W}{\partial \mathbf{u}_{\beta s}} \cdot \dot{\mathbf{u}}_{\beta s} + J \sum_{\beta=1,+,0} \left[ \mathbf{v}_{\beta s} \cdot \left( \mathbf{\dot{\zeta}}_\beta + \mu_\beta^e \nabla \left( \frac{n_\beta \rho_\beta}{\rho_\beta^0} \right) \nabla \psi_\beta \right) \right] \right] \geq 0
$$

with the 'effective' electro-chemical potential of the ions:

$$
\mu_\beta^e = \mu_\beta , \text{ and } \mu_i^e = \mu_i + \frac{z_i}{V_i} \lambda ,
$$

herein, the chemical potentials, $\mu_\beta$ are defined as:

$$
\mu_\beta = \frac{\partial W}{\partial \dot{\zeta}_\beta} .
$$

The non-dissipative part $\Phi_R$ (49) is a linear function of the group of constitutive variables:

$$
\nabla \mathbf{v}_s, \nabla \mathbf{v}_{\beta s}, \dot{\mathbf{u}}_{\beta s}
$$

which, are neither independent nor dependent variables. Because inequality (49) holds for all values of the variables (52), the coefficients of the terms which are linear in these variables vanish for all values of the independent variables (42). Each of these terms are therefore zero. The resulting relationships are:

$$
\frac{\partial W}{\partial \mathbf{u}_{\beta s}} = \mathbf{0} ,
$$

$$
\mathbf{\sigma}_\beta = \left[ \psi_\beta - \frac{n_\beta \rho_\beta}{\rho_\beta^0} \mu_\beta^e \right] \mathbf{1} ,
$$

(54)
As a result of equation (53), the strain energy function $W$ cannot depend on the relative velocities. According to equation (55) the total stress of the mixture is derived from the strain energy function $W$, which physically has the same meaning as in a single component medium. The principle of equipresence results in an stress-strain relationship in which $T$ depends also on the compressibility of the solid and the fluid through $\zeta_1$ and on the local ion concentration via $\zeta_+$ and $\zeta_-$. 

As a measure of referential stress, the second (symmetric) Piola-Kirchhoff stress tensor $T$ is introduced:

$$ T = J F^{-1} \cdot \sigma \cdot F^c, \quad (56) $$

and rewriting equation (55) yields:

$$ T = \frac{\partial W}{\partial E_s}. \quad (57) $$

The remaining part of the extended entropy inequality (39), reads:

$$ J \sum_{\beta=\pm} [v_{b\beta} \cdot (-\hat{\pi}_\beta + \mu_{\beta} \nabla \left( \frac{n_\beta \rho_\beta}{\rho_\beta^0} \right) - \nabla \psi_\beta)] \geq 0. \quad (58) $$

Substitution of the constitutive laws (54) and transforming the relative velocities to their Lagrangian equivalents, yields:

$$ -J \sum_{\beta=\pm} [u_{b\beta} \cdot \left( \frac{n_\beta \rho_\beta}{\rho_\beta^0} \right) \nabla_0 \mu_{\beta}^c] \geq 0. \quad (59) $$

The rate of entropy dissipation is thus determined by scalar products of the driving forces $\nabla_0 \mu_{\beta}^c$ and the dual dissipative fluxes $u_{b\beta}$. The summation of these scalar products is always negative and for non-trivial (non-equilibrium) values this can only hold if the
driving forces and the dissipative fluxes are functionally related. We assume that they are linearly related:

\[
\frac{J_{n_\beta} \rho_{\beta}}{\rho_{\beta}^0} \nabla_\gamma \mu_{\gamma} = -\mathbf{B}_{\beta \gamma} \cdot \mathbf{u}_\gamma
\]

In which \( \mathbf{B}_{\beta \gamma} \) is a positive definite frictional tensor.

V. Discussion: Linear Constitutive Equations

The energy function \( W = W(E_s, \zeta_\beta) \) is assumed to be a continuously differentiable function. By expanding the function \( W \) in a Taylor series, using only the linear and the quadratic terms, the constitutive laws are recasted in their differentiated form:

\[
\begin{bmatrix}
T \\
\dot{\mu}_\beta
\end{bmatrix} = 
\begin{bmatrix}
E_s \\
\dot{\zeta}_\beta
\end{bmatrix}
\]

\[
C
\]

herein, \( C \) is the matrix containing the second order derivatives of the strain energy function \( W \) with respect to the variables \( E_s, \zeta_\beta \). The matrix \( C \) is symmetric and its form is discussed in detail in [28] in the case of a linear anisotropic fluid-solid mixture. The exact form of the function \( W \) is to be derived from experiments and is beyond the scope of this paper.

In some cases, the constitutive laws described by equation (61) can be simplified through the procedure of physical and geometrical linearization. The physical linearization involves the assumption that the response coefficients are material constants. The geometrical linearization consists in assuming infinitesimal deformations:

\[
\mathbf{F} = \mathbf{I} + \delta \mathbf{F}
\]
in which only linear contributions of $\delta F$ are taken into account. Because this aspect of the linearization is non-trivial in mixtures, it is discussed in more detail. Except that in infinitesimal theory is assumed small with respect to the unit tensor, there are notational problems in switching for mixture theory to infinitesimal poromechanics. These notational problems stem from inconsistencies in notation between finite deformation theory and infinitesimal theory (Table 1). In essence they are the consequence of the convention that in infinitesimal theory $\mathbf{x}$ refers to the initial position of a particle, while in finite deformation theory (and in fluid mechanics, and in mixture theory) $\mathbf{x}$ refers to the current position of a particle. Hence, even if there is unanimity about what the displacement $\mathbf{u}$ is, the function $\mathbf{u}(\mathbf{x},t)$ is essentially a different function in both theories because $\mathbf{x}$ stand for a different quantity. The partial time derivative $\frac{\partial}{\partial t}$ is the time derivative in which $\mathbf{x}$ is held constant. But as $\mathbf{x}$ is the initial position vector in infinitesimal theory, the partial time derivative stand for the material time derivative, which is a semantic conflict with fluid mechanics, mixture theory and finite deformation theory. This is the reason why Biot [12] typically writes velocity as $\frac{\partial \mathbf{u}}{\partial t}$ while Bowen [23] writes velocity as $\frac{D\mathbf{u}}{Dt}$.

Unlike what is often thought the material time derivative and the spatial time derivative are essentially different in infinitesimal theory. Indeed there is no reason why the convective term in

$$\frac{D}{Dt} = \frac{\partial}{\partial t} + \mathbf{v} \cdot \nabla$$

would vanish in infinitesimal theory. Taking for instance the mass balance of the streaming constituents (47):
\[ \dot{m}_\beta + J \nabla \cdot (n_\beta \rho_\beta v_{\beta s}) = 0 \]  
\[ (63) \]

And transforming this equation back to the initial configuration, one finds

\[ \frac{D' m_\beta}{Dt} + \nabla_0 \cdot F^{-1} m_\beta v_{\beta s} = 0 \]  
\[ (64) \]

Dividing by the initial density of the constituent \( \rho_\beta^0 \), one finds:

\[ \frac{D' \xi^\beta}{Dt} + \nabla_0 \cdot \xi^\beta u_{\beta s} = 0 \]  
\[ (65) \]

If we now use the notational transformation described in Table 1, and neglect all quadratic contributions of \( \delta F \), we find the infinitesimal form the mass balance:

\[ \frac{\partial \xi^\beta}{\partial t} + \nabla \cdot (v^\beta - v_s) = 0 . \]  
\[ (66) \]

Eq. (68) is well known from the papers of Biot. For instance, it is the time differentiated form of the equation \( \zeta = -\text{div} \mathbf{w} \) appearing below eq. (2.1) in [29]. Note that at first sight Eq. (68) is in conflict with the original mass balance equation (21). There is no conflict because \( \frac{\partial}{\partial t} \) and \( \nabla \) have a different meaning in both equations. The Green-Lagrange strain tensor \( \mathbf{E}_s \) reduces to the infinitesimal strain tensor \( \mathbf{\varepsilon}_s \):

\[ \mathbf{E}_s = \varepsilon_s = \frac{1}{2}(\delta F + \delta F^T) \]

The jacobian \( J \) reduces to

\[ J = 1 + \text{tr} \varepsilon_s , \]

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<th>Finite deformation theory</th>
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<tr>
<td>Initial position</td>
<td>X</td>
<td>x</td>
</tr>
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</table>
Table 1: Finite deformation theory and infinitesimal theory have conflicting notation conventions.

Momentum balance keeps the same form:

\[ \nabla \cdot \sigma = 0 \]  

The frictional equation turns into

\[ \zeta_{\beta} \nabla \mu_{\beta} = -B_{\rho_j} \cdot (v_{\gamma} - v_{s}) \]  

Further simplification of the constitutive laws is obtained by assuming isotropic material behaviour. A simple form of \( W \) that combines linear isotropic poro-elasticity with classical Donnan-osmosis is:

\[ W = \mu_s \varepsilon : \varepsilon + \frac{1}{2} (\lambda_s + \alpha^2 M)(\text{tr} \varepsilon)^2 + \sum_{\beta=1,\ldots} \left[ -\alpha M (\text{tr} \varepsilon)(\zeta_{\beta} - \zeta_{\beta_0}) + \frac{1}{2} M (\zeta_{\beta} - \zeta_{\beta_0})^2 \right] \]

\[ + RT \sum_{i=s,v} \left[ \frac{\zeta_i}{V_i} (\ln \xi_i - \ln \xi_f - 1) \right] \]  

herein, \( \alpha \) and \( M \) are the two additional Biot coefficients to the classical elastic constants \( \lambda_s \) and \( \mu_s \), describing the coupling between the solid and fluid stress and
strain, \( R \) is the universal gas constant and \( T \) is the absolute temperature. \( \zeta_{\beta 0} \) is the initial values of the unstrained volume fractions.

Equation (69) results in the following expressions for the stress:

\[
\sigma = \lambda \varepsilon + 2 \mu \varepsilon + \alpha I (\alpha M \varepsilon - M \sum_{\beta=L,+,\ldots} (\zeta_{\beta} - \zeta_{\beta 0}))
\]  

(70)

The expression for the stress is identical to the classical Biot expression, except that the fluid content is replaced by the sum of fluid and ionic content. The expression for the fluid (electro)-chemical potential following form (69) reads:

\[
\mu_i = -\alpha M \varepsilon + M \sum_{\beta=L,+,\ldots} (\zeta_{\beta} - \zeta_{\beta 0}) - \frac{RT}{\zeta_f} \sum_{i=+,\ldots} C_i ,
\]  

(71)

which is the difference between the pressure \( p \) and the osmotic pressure \( \Pi \):

\[
p = -\alpha M \varepsilon + M \sum_{\beta=L,+,\ldots} (\zeta_{\beta} - \zeta_{\beta 0}) , \quad \text{and} \quad \Pi = \frac{RT}{\zeta_f} \sum_{i=+,\ldots} C_i .
\]  

(72)

The osmotic pressure \( \Pi \) is consistent with the classical van ‘t Hoff expression [1,30].

The electro-chemical potentials of the ions following from (69) yield the well-known expressions from electro-chemistry [1]:

\[
\overline{\nu} \mu_i = p \overline{\nu} + RT \ln \left( \frac{C_i}{\zeta_f} \right) + \zeta F \xi ,
\]  

(73)

herein, the Lagrange multiplier \( \lambda \) (see (50)) is identified as the Faraday constant \( F \) times the electrical-potential \( \xi \) and realising that the presented electro-chemical potentials are per unit initial volume, while they are usually expressed per unit mole.

**Example: viscous drag flow in ionised medium**

Consider a cylindrical, linear elastic ionised sample enclosed in a tightly fitting rigid jacket (fig. 1). The right side of the sample (\( x=L \)) is resting on a filter saturated with a
physiological NaCl solution (c=0.15 M). The filter has a hydraulic permeability which
is assumed infinitely high compared to the hydraulic permeability of the sample. The
pressure of the fluid in the filter is 0. The left side of the sample (x=0) is in contact with
a physiological salt solution reservoir at pressure $p_0$. The sample is equilibrated with
the salt solution. We consider the steady state flow of physiological salt solution from
left to right.

Substituting eq. (68) into eq. (66) yields:

$$\frac{\partial \xi_{\beta \gamma}}{\partial t} - \nabla \cdot (K_{\beta \gamma}) \cdot \nabla \mu_{\gamma} = 0$$

(74)

In which $K_{\beta \gamma} = \xi_{\beta \gamma} (B^{-1})_{\beta \gamma}$ is the generalised permeability tensor. In steady state, the
time derivative vanishes, and if we assume that under infinitesimal deformation $K_{\beta \gamma}$ is
non-zero and constant, we find

$$\nabla^2 \mu_{\beta} = 0,$$

(75)

showing that the (electro)chemical potentials vary linearly across the sample:

$$\mu_{\beta} = (\mu_{\beta})_L + [(\mu_{\beta})_R - (\mu_{\beta})_L] \frac{x}{L}$$

(76)

With $(\mu_{\beta})_L$ and $(\mu_{\beta})_R$ are the left and right boundary conditions specified by the
physiological salt reservoirs. Integrating the momentum balance (67):

$$\sigma = -p_0$$

(77)

And substituting eq. (70), yields:

$$-p_0 = (\lambda_\kappa + 2\mu_\kappa + \alpha^2 M)\varepsilon_\kappa - M \sum_{\beta=\pm, \ldots} (\xi_{\beta} - \xi_{\beta0}).$$

(78)

Eq. (76) is substituted into eq. (71)
\[ (\mu^e_i + [(\mu^e_i), - (\mu^e_i)]) \frac{x}{L} = -\alpha M \epsilon_s + M \sum_{\beta=\alpha,\gamma} (\zeta_\beta - \zeta_{\beta_0}) - RT \sum_{i=\alpha,\gamma} \frac{\zeta_i}{\gamma_f} \] (79)

and into eq. (73):

\[ \bar{V}_i[(\mu^e_i + [(\mu^e_i), - (\mu^e_i)]) \frac{x}{L}] = (-\alpha M \epsilon_s + M \sum_{\beta=\alpha,\gamma} (\zeta_\beta - \zeta_{\beta_0}))\bar{V}_i + RT \ln \left( \frac{\zeta_i}{\gamma_f} \right) + \zeta_i F \] (80)

Electroneutrality (36) requires that:

\[ C^k + \frac{\zeta_+}{V_+} - \frac{\zeta_-}{V_-} = 0 \] (81)

Eqs. (78-81) are a set of 5 equations with 5 unknowns: \( \epsilon_s, \zeta_f, \zeta_+, \zeta_- \) and \( \xi \) and are solved for a sample of thickness \( L=1 \) mm, equilibrated in a physiological NaCl solution of 0.15 M. The fixed charge density per unit initial mixture volume is \( C^k = -0.02 \) mol/l, the initial fluid volume fraction \( \zeta_f / _0 = 0.1 \), the storage modulus \( M=200 \) MPa, the Lame constants are \( \mu = 100 \) MPa and \( \lambda = 150 \) MPa. The Biot coefficient \( \alpha \) is varied. The sample is subject to a pressure boundary condition of \( p_0 = 0.1 \) MPa on the lefthandside. The steady state flow conditions developing as a result of the pressure gradient is considered. The resulting strain, fluid volume fraction, cationic volume fraction and anionic volume fractions are plotted in figure 2. Figure 3 shows the same plots for \( M=200 \) GPa except for the strain, because the strain is not affected by the value of the storage modulus \( M \).

**Discussion**

A generalisation of Biot’s poro-elasticity theory to ionised porous media is derived from mixture theory. The formulation includes both concentration and electro-chemical effects. Streaming currents, streaming potentials, diffusion currents, diffusion...
potentials, electrophoresis, electro-osmosis, Donnan osmosis, Donnan potential, Donnan exclusion, chemical osmosis are phenomena described by the presented equations.

The corresponding incompressible theory has been presented earlier [3]. The derivation is done from mixture theory, but using independent and dependent constitutive variables as used by Biot [21]. Except that Bowen does not consider electrical effects, our approach differs significantly from Bowen [24]. In the approach presented in this paper, the principle of equipresence is strictly adhered to, while Bowen deliberately violates the principle, in his view ‘to avoid too elaborate mathematics’. In Eq. 3.1 [24], Bowen assumes the partial free energies not to depend on the relative velocities, while from Darcy’s law, it is obvious that relative velocities should be part of either the dependent or the independent constitutive variables. In this paper, the equations and the inequality are transformed to Lagrangian variables, leading to the important result (53) that the total free energy cannot depend on the relative velocities, by virtue of the second law. Therefore here, this independence from velocities is not an assumption, but a requirement from first principles. A consequence of this result is, that total stress and (electro)chemical potentials cannot depend on relative velocities by virtue of equations (51) and (55). The constitutive relationships for stress and (electro)chemical potentials are therefore significantly simplified, as the velocities represent three vectorial quantities. Because the momentum interaction between constituents definitely depends on relative velocities, it seems even unlikely that partial energies and stress be independent from relative velocities and therefore the results obtained for the partial free energies \( \Psi_\beta \) are not the same as Bowen, nor for the partial stresses \( \sigma_\beta \) nor for the momentum interaction \( \dot{\mathbf{r}}_\beta \). The constitutive relationships for the partial stresses, partial energies and momentum interactions are, however, only of academic value as they are
not needed for the solution of practical problems. Biot [21] assumes intuitively – without justification – that the total free energy $W$ of the mixture does not depend on relative velocities.

The concentrations in the expressions of electrochemical potentials are done in terms of molar concentration per unit fluid volume in incompressible theories [2,3]. In the case of a compressible fluid, this fluid volume depends on pressure. Here, the concentrations are defined as ratios of masses which is more consistent with experiments than volumetric concentrations. [30]

The classical mass balance used by Biot is derived from mixture theory. It is demonstrated that the inconsistency between mass balances of poromechanics and mixture theory is no more than a semantic problem. This emphasises that accurate definitions of time derivatives and gradient operators is vital in mixture problems.

The analysis of viscous drag compression is consistent with the analysis presented by Gu et al. [31] for the limiting case of incompressible constituents ($\alpha = 1$ and $M \rightarrow \infty$). The compressive strain distribution is independent from the storage modulus $M$.

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Notation

Subscripts

$\alpha$   constituent ($\alpha = s,f,+,-$)

$\beta,\gamma$  streaming constituent ($\beta=f,+,-$)

$i$  ionic constituent ($i = +,-$)

Symbols

$B$  the positive definite matrix containing the ‘frictional’ tensors.

$C_{fc}$  fixed charge density per unit initial mixture volume.

$C_i$  molar concentrations of the ion $i$ per unit initial mixture volume.

$D_i^0$  the diffusion tensor in free solution of ion $i$.

$E_s$  solid phase strain tensor

$F$  Faraday’s constant

$J$  relative volume change from the initial state to the current state.

$K$  the ‘permeability’ tensors

$M$  storage modulus$_\alpha$

$N_{\alpha}$  number of mol of constituent $\alpha$

$R$  universal gas constant.

$T$  absolute temperature.

$V$  representative elementary volume
\( \bar{V}_\beta \) molar volume of the constituent \( \beta \)

\( W \) strain energy function

\( c_i \) (internal) dimensionless concentrations

\( e_\alpha \) partial internal energy of the \( \alpha \)th constituent per unit constituent mass

\( h_\alpha \) partial heat

\( m_\alpha \) mass of constituent \( \alpha \) per unit undeformed solid volume

\( n_\alpha \) volume fraction of the constituent \( \alpha \)

\( p \) pore pressure

\( q_\alpha \) heat flux of the constituent \( \alpha \)

\( r_i \) the ‘apparent hindrance factor’ of the ion \( i \)

\( v_\alpha \) velocity of the \( \alpha \)th constituent

\( v_\beta \) velocity of the \( \beta \)th component relative to the solid component

\( z_i \) valences of the ionic species

\( \Phi \) dissipation function (with \( \Phi_i \) the irreversible part and \( \Phi_k \) the reversible part)

\( \Psi_\alpha \) Helmholtz free energy

\( \alpha \) Biot alfa coefficient

\( \varepsilon \) infinitesimal strain tensor of the solid

\( \gamma \) bulk density of the mixture

\( \zeta_\beta \) unstrained volume fraction constituent \( \beta \).

\( \eta_\alpha \) entropy density of \( \alpha \)th constituent.
\( \theta_\alpha \) partial temperature

\( \kappa \) hydraulic permeability matrix.

\( \lambda_s \) Lamé elastic constant.

\( \mu_\beta \) chemical potentials of the constituent \( \beta \)

\( \mu^e_\beta \) electro-chemical potentials of the constituent \( \beta \)

\( \mu_s \) Lamé elastic constant

\( \xi_\alpha \) entropy production.

\( \hat{\pi}_\alpha \) momentum supplied by constituents other than \( \alpha \)

\( \rho_\alpha \) intrinsic or true mass density of the \( \alpha \)th constituent

\( \sigma \) total stress tensor of the mixture

\( \Psi_\beta \) partial free energy of the constituent \( \alpha \)

References


Legends

Figure 1: Viscous drag compression: a pressure gradient is applied across a sample. The sample is supported by a porous filter. The hydraulic permeability of the porous filter is orders of magnitude larger than the hydraulic permeability of the sample.

Figure 2: Computed strain $\varepsilon$, fluid content $\zeta_f$, cationic content $\zeta^+$, anionic content $\zeta^-$ and electrical potential $\xi$ as a function of depth $x$ for a viscous drag experiment. Continuous line $\alpha = 0.6$, dashed line $\alpha = 0.8$, ***** $\alpha = 1$. Storage modulus $M=200$ MPa.

Figure 3: Computed fluid content $\zeta_f$, cationic content $\zeta^+$, anionic content $\zeta^-$ and electrical potential $\xi$ as a function of depth $x$ for a viscous drag experiment. Continuous line $\alpha = 0.6$, dashed line $\alpha = 0.8$, ***** $\alpha = 1$. Storage modulus $M=200$ GPa.
Figure 1
Figure 2