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Long-term Performance of Engineered Barrier Systems PEBS

Extrapolation of the models developed to the repository long-term evolution and evaluation of uncertainties - Review of thermomechanical continuum mixture theories applicable for EBS materials

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PEBS



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1 Introduction

In the first PEBS-deliverable (D3.3-2) an overview of the modeling tasks in the Swedish safety assessment modeling report that included bentonite buffer was given. Descriptions, main results, and discussions about issues related to uncertainties/limitations/inadequacies in material representations were given for modeling tasks considered most relevant for the PEBS framework. The discussed issues considered,

- Retention: its lack of coupling to mechanics, and its lack of path dependence.
- Water transportation: for which the actual driving force/real mechanism is questioned to be represented in the present type of models.
- Mechanical representation: which was found to have limited range of validity, strong process dependence, and was designed for *typical* geomaterials and not for *atypical* geomaterials (clayey swelling materials with montmorillonite as the governing constituent).

As can be seen from studying the listed items above several of the issues relate to a lack of generality and couplings in the used models. Also, for the systems we consider, good agreement has commonly been obtained between theories based on thermodynamical/chemical considerations and experimental findings, e.g. (Low and Anderson, 1958), (Oliphant and Low, 1982), (Kahr et al., 1990), (Karlund et al., 2005), (Birgersson et al., 2008), and (Birgersson and Karlund, 2009).

Therefore, as a step towards addressing the listed issues, it is of interest to study general continuum theories for mixtures which use thermodynamics and mechanics (thermomechanics in short) as a basis and intrinsically allows for various couplings and incorporation of chemical reactions.

The framework of thermomechanical mixture theories contains classical “engineering” soil mechanics formulations which we currently use when modeling our system. Therefore, we may by studying the more general framework get a new perspective of the “engineering” soil mechanics formulations and the concepts used therein.

The objectives of the material presented here are to give an introduction and overview of a thermomechanical continuum theory of mixtures, describe some proposals of constitutive relations fitting into this framework, and try to study the basis of some concepts used in “engineering” soil mechanics formulations.

These notes are initialized with a brief orientation about continuum mixture theory as a warm up of what is to come. This is followed by a short repetition of continuum thermomechanics for a single component body, in order to set the stage and introduce notation. Thereafter, an outline of the main structure of the general theory is followed by notes taken when studying existing constitutive laws within the mixture theory framework in an attempt to bring some light on the issues listed above. A schematic proposal of a material model structure for bentonite buffer is then given in terms of a concept which is called non-associative immiscibility. Finally, summary and concluding remarks are given.

2 Short orientation about continuum mixture theory

To begin with it should be clear that this report address continuum mixture theory with its basis in *Rational thermodynamics* as first described by Truesdell in 1957 and later on in (Truesdell, 1984), a reference I have used a lot. There are more modern mixture theory formulations, but since I was somewhat familiar with Rational thermodynamics beforehand it was natural to stick with this.

Continuum mixture theory is a macroscopic representation of the thermomechanical behavior of a material body consisting of a mixture of several constituents, i.e. a multi-component formulation. The framework is capable of incorporating diffusion, phase transition, and chemical reactions in the broadest sense.

In 1957, Truesdell was the first to cast continuum mixture theory in modern form. At this time, what was still lacking was a proper formulation of the entropy inequality and an insight of how to use this in the theoretical framework. The prerequisite for this came with Coleman and Noll's work treating single materials presented in 1963. After several propositions had been published for mixtures in the following years, all of which, however, turned out to have severe defects when trying to represent fluid mixtures, Müller was in 1968 the first who presented a workable form of the second law and also pointed out that density gradients should be taken as one of the independent variables introduced in the constitutive relations in order to obtain a theory that was in agreement with classical thermochemistry.

Other influential contributors to the field are Bowen, Kelly, Hutter, Gurtin and Liu. The work of Bowen is much directed towards the traditional immiscible formulations used in soil mechanics with a porous solid penetrated by fluids. We are going to use models proposed by Bowen to study some concepts present in the "engineering" soil mechanics formulations.

In the multi-component formulation, constituents are simultaneously occupying every material point. It can be thought of as representing the mixture with a number of superimposed continua, each of which represent a constituent. The constituent continua may locally be regarded open systems undergoing thermomechanical exchanges with the other constituent continua. The exchanges are manifested through introduced production terms in the five balance relations for the individual constituents concerning; mass, linear momentum, angular momentum, energy, and entropy. The constituent relations are however not formulated as conservation equations. The axioms of conservation for the mixture are instead formulated as sums of the corresponding production terms, vanishing for all axioms except for the entropy production which should be non-negative.

There are significant differences between the obtained multi-component formulation as compared to single component theories. If "mixture quantities" are formed, in addition to sums of corresponding constituent quantities, terms including velocity differences will contribute. The "mixture stress" (total stress) has for instance contributions from velocity differences. One fundamental difference is that the relation between the total energy flux and entropy flux is not the same. This comes from an additional contribution to the energy flux due to diffusion. This diffusive energy flux can be formulated in terms of chemical potentials of the constituents.

Chemical potentials are quantities naturally appearing within the multi-component framework. When there is diffusion (or more generally, difference in velocities between constituents), chemical potentials will provide a contribution to the total energy flux besides the heat flux. Using the concept of semi-permeable membrane, the chemical potential for a specific

constituent in a mixture may be defined as: the quantity that is continuous across a membrane only permeable for that constituent.

In its original, and most general form, mixture theory considers miscible constituents, i.e. the constituents form a homogeneous mixture at a fine scale. Additional constraints, however, allows incorporation of immiscibility between constituents. As a result from the immiscibility the material obtains a microstructure which is manifested through volume fractions of the constituents. This concept is often used when studying mixtures of porous media. Immiscible mixture theory formulations can often be simplified to a form which coincides with classical theories of porous media.

So, above, the general framework has been described, but to close the problem, constitutive relations must be formulated where dependent variables are given by functions of independent variables. It is in this step which characteristic behaviors of the material system are to be introduced. In the constitutive laws, couplings between different constituents may be introduced to different degree, in terms of no-way, one-way, and two-way couplings. Often, to begin with, quite general constitutive relations are prescribed where extensive dependencies are allowed and then, the entropy inequality are used to reduce the number of dependent variables and put restrictions on the constitutive relations.

3 Continuum thermomechanics for a single component body

Continuum thermomechanics for a single component body is first reviewed in order to set the stage for the multi-component theory and introduce the notation. We have a continuous body B of material points $P \in B$, with position x at time t given by the motion χ according to,

$$x = \chi(P, t),$$

which is invertible such that $P = \chi^{-1}(x, t)$. For a referential configuration at time t_R the position for the point is given by

$$X = \chi(P, t_R) = \chi_R(P),$$

which also is invertible such that $P = \chi_R^{-1}(X)$. Using that P may be identified by X and ignoring the distinction we may write

$$x = \chi(X, t).$$

The deformation gradient F relates increments dx and dX according to,

$$dx = FdX = (\text{GRAD}x)dX.$$

The velocity is defined by,

$$v = \partial_t \chi(X, t) = v(x, t),$$

and the acceleration by,

$$\dot{v} = \partial_t^2 \chi(X, t) = \dot{v}(x, t).$$

Variable fields are introduced as primitive entities when formulating the five axioms of thermomechanics. The fields are:

$\rho = dm/dv$: mass density, dm is the mass element of the volume element dv ,

T : Cauchy stress,

b : body force,

q : energy (heat) flux,

r : energy (heat) supply,

ε : specific internal energy,

η : specific entropy,

Φ : entropy flux,

σ : entropy supply,

γ : entropy production,

θ : absolute temperature ($\theta > 0$),

$\psi = \varepsilon - \theta\eta$: Helmholtz free energy.

As can be seen, index free notation is used, so for clarity definitions of operators are given below for orthonormal bases $\{\mathbf{E}_J\}$ and $\{\mathbf{e}_j\}$ in the referential and current configuration, respectively.

$\text{grad}\phi = \partial\phi / \partial x_j \mathbf{e}_j$, $\text{grad}\mathbf{v} = \partial v_i / \partial x_j \mathbf{e}_i \otimes \mathbf{e}_j$, $\text{GRAD}\mathbf{v} = \partial v_i / \partial X_J \mathbf{e}_i \otimes \mathbf{E}_J$, $\text{div}\mathbf{v} = \partial v_i / \partial x_i$,
 $\text{div}\mathbf{T} = \partial T_{ij} / \partial x_j \mathbf{e}_i$, $\text{GRAD}\mathbf{F} = \partial F_{ij} / \partial X_K \mathbf{e}_i \otimes \mathbf{E}_j \otimes \mathbf{E}_K$, $\mathbf{A} \cdot \mathbf{B} = A_{ij} B_{ij}$

3.1 Axioms in global form

The five axioms of thermomechanics for a single component body are listed below in global form.

Conservation of mass:

$$\partial_t \left(\int \rho \, dv \right) = 0$$

Conservation of linear momentum:

$$\partial_t \left(\int \rho \mathbf{v} \, dv \right) - \oint \mathbf{T} \mathbf{n} \, dA - \int \rho \mathbf{b} \, dv = \mathbf{0}$$

Conservation of rotational momentum:

$$\partial_t \left(\int \Delta \mathbf{x} \times \rho \mathbf{v} \, dv \right) - \oint \Delta \mathbf{x} \times \mathbf{T} \mathbf{n} \, dA - \int \Delta \mathbf{x} \times \rho \mathbf{b} \, dv = \mathbf{0}$$

Conservation of energy:

$$\partial_t \left(\int \rho \left(\varepsilon + \frac{1}{2} v^2 \right) \, dv \right) - \oint \mathbf{v} \cdot \mathbf{T} \mathbf{n} \, dA + \oint \mathbf{q} \cdot \mathbf{n} \, dA - \int \rho \mathbf{v} \cdot \mathbf{b} \, dv - \int \rho r \, dv = 0$$

Entropy inequality:

$$\int \rho \gamma \, dv = \partial_t \left(\int \rho \eta \, dv \right) + \oint \Phi \cdot \mathbf{n} \, dA - \int \rho \sigma \, dv \geq 0$$

No assumptions have been made regarding the form of the entropy flux and entropy production. The traditional assumption is that the entropy flux and entropy production are given by the heat flux and heat supply divided by absolute temperature, $\Phi = \mathbf{q}/\theta$ and $\sigma = r/\theta$, respectively.

3.2 Axioms on local form in regular points

The five axioms expressed in global form above have corresponding local forms for *regular points* where fields are continuous.

Conservation of mass:

$$\dot{\rho} + \rho \operatorname{div} \mathbf{v} = 0$$

Conservation of linear momentum:

$$\rho \dot{\mathbf{v}} - \operatorname{div} \mathbf{T} - \rho \mathbf{b} = \mathbf{0}$$

*Conservation of rotational momentum:*¹

$$\mathbf{T} - \mathbf{T}^T = \mathbf{0}$$

Conservation of energy:

$$\rho \dot{\varepsilon} + \operatorname{div} \mathbf{q} - \rho r - \mathbf{T} \cdot \operatorname{grad} \mathbf{v} = 0$$

Entropy inequality:

$$\rho \dot{\eta} = \rho \dot{\eta} + \operatorname{div} \Phi - \rho \sigma \geq 0$$

and using $\Phi = \mathbf{q}/\theta$ and $\sigma = r/\theta$ we obtain,

$$\rho \dot{\eta} = \rho \dot{\eta} + \operatorname{div}(\mathbf{q}/\theta) - \rho r/\theta \geq 0,$$

or when using Helmholtz free energy, $\psi = \varepsilon - \theta \eta$ and conservation of energy, the *reduced dissipation inequality*,

$$\rho \dot{\psi} - \mathbf{T} \cdot \operatorname{grad} \mathbf{v} + \rho \eta \dot{\theta} + \mathbf{q}/\theta \cdot \operatorname{grad} \theta \geq 0,$$

is obtained.

¹ Here, symmetry of the stress tensor is assumed, i.e. no polar, structured, media incorporating stress couples is allowed.

3.3 Axioms on local form in singular points

The five axioms also have local forms for *singular points* belonging to a *discontinuity surface* \mathcal{S} where fields, $f(\mathbf{x}, t)$, may suffer a *jump*, defined by

$$\llbracket f \rrbracket = f^+ - f^-.$$

f^+ and f^- denote the limit values of $f(\mathbf{x}, t)$ when approaching the singular point from different side of the discontinuity surface. Letting $\mathbf{v}_\mathcal{S}(\mathbf{x}, t)$ and $\mathbf{n}_\mathcal{S}(\mathbf{x}, t)$ denote the velocity and normal of the discontinuity surface, local forms of the five axioms, so called *jump conditions*, may be derived.

Conservation of mass:

$$\llbracket \rho(\mathbf{v} - \mathbf{v}_\mathcal{S}) \rrbracket \cdot \mathbf{n}_\mathcal{S} = 0$$

Conservation of linear momentum:

$$\llbracket \rho \mathbf{v}(\mathbf{v} - \mathbf{v}_\mathcal{S}) \cdot \mathbf{n}_\mathcal{S} - \mathbf{T} \mathbf{n}_\mathcal{S} \rrbracket = \mathbf{0}$$

Conservation of rotational momentum:

$$\llbracket \Delta \mathbf{x} \times (\rho \mathbf{v}) \otimes (\mathbf{v} - \mathbf{v}_\mathcal{S}) - \Delta \mathbf{x} \times \mathbf{T} \rrbracket \mathbf{n}_\mathcal{S} = \mathbf{0}$$

Conservation of energy:

$$\llbracket \rho \left(\varepsilon + \frac{1}{2} \mathbf{v}^2 \right) (\mathbf{v} - \mathbf{v}_\mathcal{S}) + \mathbf{q} - \mathbf{T} \mathbf{v} \rrbracket \cdot \mathbf{n}_\mathcal{S} = 0$$

Entropy inequality:

$$\llbracket \rho \eta (\mathbf{v} - \mathbf{v}_\mathcal{S}) + \Phi \rrbracket \cdot \mathbf{n}_\mathcal{S} + \gamma_\mathcal{S} \geq 0,$$

where $\gamma_\mathcal{S}$ is an entropy production per unit surface. Using $\Phi = \mathbf{q}/\theta$ we obtain,

$$\llbracket \rho \eta (\mathbf{v} - \mathbf{v}_\mathcal{S}) + \mathbf{q}/\theta \rrbracket \cdot \mathbf{n}_\mathcal{S} + \gamma_\mathcal{S} \geq 0.$$

3.4 General constitutive laws

A *thermomechanical process* is given by the set of nine functions:

$$\chi(\mathbf{X}, t), \theta(\mathbf{x}, t), \rho(\mathbf{x}, t), \mathbf{T}(\mathbf{x}, t), \psi(\mathbf{x}, t), \mathbf{q}(\mathbf{x}, t), \eta(\mathbf{x}, t), \mathbf{b}(\mathbf{x}, t) \text{ and } r(\mathbf{x}, t),$$

obeying the four conservation laws. To close the problem formulation, *constitutive relations*, expressing specific material characteristics, must be formulated. Commonly, conservation of mass, conservation of linear momentum, and conservation of energy, are used to determine the fields

$$\rho(\mathbf{x}, t), \mathbf{b}(\mathbf{x}, t), \text{ and } r(\mathbf{x}, t),$$

respectively, so that the balance laws always are fulfilled given the other fields. Usually,

$\chi(\mathbf{X}, t)$ and $\theta(\mathbf{x}, t)$

are selected as *independent variables* and

$\mathbf{T}(\mathbf{x}, t)$, $\psi(\mathbf{x}, t)$, $\mathbf{q}(\mathbf{x}, t)$, and $\eta(\mathbf{x}, t)$

as the *dependent variables* to be determined from the independent by the constitutive relations. This may formally be written using a *response function* f ,

$$(\mathbf{T}(\mathbf{x}, t), \psi(\mathbf{x}, t), \mathbf{q}(\mathbf{x}, t), \eta(\mathbf{x}, t)) = f(\chi(\cdot, \cdot), \theta(\cdot, \cdot)).$$

An *admissible thermomechanical process* is a thermodynamic process which is consistent with the response function.

So far, the entropy inequality has not been involved, but the entropy inequality is now to serve as a constraint to be fulfilled by the solutions obtained from the conservation laws. One may use the entropy inequality as a direct restriction on $\chi(\mathbf{X}, t)$ and $\theta(\mathbf{x}, t)$ or as a constraint when designing the response function f , so that the obtained responses always are fulfilling the inequality.

To my knowledge, the most common way is to do the latter, to use the entropy inequality when formulating the constitutive relations, so that the condition always is fulfilled for all admissible thermomechanical processes. Coleman and Noll proposed a procedure in 1963 where the entropy inequality is used as a constraint on the response function and a more recent method is according to Müller in 1971, where the admissible thermomechanical processes act as restrictions of the entropy inequality.

4 Continuum thermomechanics for a multi-component body

The formulation given below is similar to that of Truesdell, Bowen, and early works of Müller where all constituents α , $\alpha = 1 \dots N$, have a common temperature $\theta_\alpha = \theta > 0$. When formulating the *Theory of diffusion*, as Truesdell (1984) denote it, he lay down following three metaphysical principles (Truesdell 1984):

1. *All properties of the mixture must be mathematical consequences of properties of the constituents.*
2. *So as to describe the motion of a constituent, we may in imagination isolate it from the rest of the mixture, provided we allow properly for the actions of the other constituents upon it.*
3. *The motion of the mixture is governed by the same equations as it is a single body.*

The kinematics given below is described differently as compared to Bowen but in accordance with Haupt (2002) and Wilmanski (2011). Wilmanski (2011) points out that Bowen does not formulate this part correctly.

For each constituent α , a velocity field,

$$\mathbf{v}_\alpha = \mathbf{v}_\alpha(\mathbf{x}, t),$$

is introduced. Just for clarity, we notice that by solution of the equations,

$$d\mathbf{x}/dt = \mathbf{v}_\alpha(\mathbf{x}, t), \quad \mathbf{x}(t = 0) = \mathbf{X}_\alpha, \quad \alpha = 1, \dots, N,$$

trajectories of constituent material particles, identified by their referential position \mathbf{X}_α , may be obtained.

Partial mass densities of constituents,

$$\rho_\alpha = \frac{dm_\alpha}{dv},$$

are introduced. dm_α is the mass of constituent α , within the volume element dv . The total mass density of the mixture is defined as

$$\rho = \sum \rho_\alpha,$$

where $\alpha = 1 \dots N$ in the summation. This notation, giving the range for the index, will be used in the forthcoming. The mixture velocity equal the barycentric velocity,

$$\mathbf{v} = 1/\rho \sum \rho_\alpha \mathbf{v}_\alpha.$$

The difference between the constituent velocity and mixture velocity defines the diffusion velocity,

$$\mathbf{u}_\alpha = \mathbf{v}_\alpha - \mathbf{v}.$$

With the above given, similar to what was done for the single media body, the remaining variable fields are introduced as primitive entities. The open system formulation of the individual constituent is manifested by incorporating exchange possibilities between constituents in form of production terms of mass, m_α^+ , linear momentum, \mathbf{m}_α^+ , angular momentum, \mathbf{M}_α^+ , energy, e_α^+ , and entropy, γ_α^+ .

4.1 Constituent balance laws on local form in regular points

For some of the balances two alternative, but in principle equal, formulations are given.

Balance of mass:

$$\dot{\rho}_\alpha + \operatorname{div}(\rho_\alpha \mathbf{v}_\alpha) = m_\alpha^+, \text{ or}$$

$$\dot{\rho}_\alpha + \rho_\alpha \operatorname{div} \mathbf{v}_\alpha = m_\alpha^+$$

Balance of linear momentum:

$$\partial_t(\rho_\alpha \mathbf{v}_\alpha) - \operatorname{div}(\mathbf{T}_\alpha - \rho_\alpha \mathbf{v}_\alpha \otimes \mathbf{v}_\alpha) - \rho_\alpha \mathbf{b}_\alpha = \mathbf{m}_\alpha^+, \text{ or}$$

$$m_\alpha^+ \mathbf{v}_\alpha + \rho_\alpha \dot{\mathbf{v}}_\alpha - \operatorname{div} \mathbf{T}_\alpha - \rho_\alpha \mathbf{b}_\alpha = \mathbf{m}_\alpha^+$$

Balance of rotational momentum:

$$\mathbf{T}_\alpha - \mathbf{T}_\alpha^T = \mathbf{M}_\alpha^+$$

Balance of energy:

$$\partial_t(\rho_\alpha \varepsilon_\alpha + \frac{1}{2} \rho_\alpha v_\alpha^2) + \operatorname{div}(\rho_\alpha (\varepsilon_\alpha + \frac{1}{2} v_\alpha^2) \mathbf{v}_\alpha - \mathbf{T}_\alpha^T \mathbf{v}_\alpha + \mathbf{q}_\alpha) - \rho_\alpha (\mathbf{b}_\alpha \cdot \mathbf{v}_\alpha + r_\alpha) = e_\alpha^+, \text{ or}$$

$$m_\alpha^+ \cdot \mathbf{v}_\alpha + m_\alpha^+ (\varepsilon_\alpha - \frac{1}{2} v_\alpha^2) + \rho_\alpha \dot{\varepsilon}_\alpha - \mathbf{T}_\alpha^T \cdot \operatorname{grad} \mathbf{v}_\alpha + \operatorname{div} \mathbf{q}_\alpha - \rho_\alpha r_\alpha = e_\alpha^+$$

Balance of entropy:

$$\partial_t(\rho_\alpha \eta_\alpha) + \operatorname{div}(\rho_\alpha \eta_\alpha \mathbf{v}_\alpha + \mathbf{q}_\alpha / \theta) - \rho_\alpha r_\alpha / \theta = \gamma_\alpha^+, \text{ or}$$

$$m_\alpha^+ \eta_\alpha + \rho_\alpha \dot{\eta}_\alpha + \operatorname{div}(\mathbf{q}_\alpha / \theta) - \rho_\alpha r_\alpha / \theta = \gamma_\alpha^+$$

4.2 Mixture conservation laws

The *conservation laws of the mixture* are given by the sums of the production terms. These are also called the *axioms of balance for mixtures*.

$$\text{Conservation of mass: } \sum m_\alpha^+ = 0$$

$$\text{Conservation of linear momentum: } \sum \mathbf{m}_\alpha^+ = \mathbf{0}$$

Conservation of rotational momentum: $\sum \mathbf{M}_\alpha^+ = \mathbf{0}$

Conservation of energy: $\sum e_\alpha^+ = 0$

Entropy inequality: $\sum \gamma_\alpha^+ \geq 0$

4.3 Mixture conservation laws on local form in regular points

If the balance laws of the constituents are used together with the conservation laws of the mixture following local conservation laws for the mixture can be formulated. The conservation laws for the mixture in terms of *mixture fields* are very similar to those of a single component body:

Conservation of mass: $\dot{\rho} + \rho \operatorname{div} \mathbf{v} = 0$

Conservation of linear momentum: $\rho \dot{\mathbf{v}} - \operatorname{div} \mathbf{T} - \rho \mathbf{b} = \mathbf{0}$

Conservation of rotational momentum: $\mathbf{T} - \mathbf{T}^T = \mathbf{0}$

Conservation of energy: $\rho \dot{\varepsilon} + \operatorname{div} \mathbf{q} - \rho r - \mathbf{T} \cdot \operatorname{grad} \mathbf{v} = 0$

Entropy inequality: $\rho \dot{\eta} + \operatorname{div} \Phi - \rho \sigma \geq 0$

The local conservation laws for the mixture as given above are expressed in the following mixture fields:

$$\mathbf{T} = \sum \mathbf{T}_\alpha - \sum \rho_\alpha \mathbf{u}_\alpha \otimes \mathbf{u}_\alpha ,$$

$$\mathbf{b} = \sum \frac{\rho_\alpha}{\rho} \mathbf{b}_\alpha ,$$

$$\varepsilon = \varepsilon^I + \frac{1}{2} \sum \frac{\rho_\alpha}{\rho} u_\alpha^2 = \sum \frac{\rho_\alpha}{\rho} \varepsilon_\alpha + \frac{1}{2} \sum \frac{\rho_\alpha}{\rho} u_\alpha^2 ,$$

$$\mathbf{q} = \sum \mathbf{q}_\alpha + \theta \sum \rho_\alpha \eta_\alpha \mathbf{u}_\alpha + \sum \mathbf{C}_\alpha^T \mathbf{u}_\alpha ,$$

$$r = \sum \frac{\rho_\alpha}{\rho} r_\alpha + \sum \rho_\alpha \mathbf{b}_\alpha \cdot \mathbf{u}_\alpha ,$$

$$\eta = \sum \frac{\rho_\alpha}{\rho} \eta_\alpha ,$$

$$\Phi = (\sum \mathbf{q}_\alpha + \theta \sum \rho_\alpha \eta_\alpha \mathbf{u}_\alpha) / \theta = (\mathbf{q} - \sum \mathbf{C}_\alpha^T \mathbf{u}_\alpha) / \theta , \text{ and}$$

$$\sigma = \left(\sum \frac{\rho_\alpha}{\rho} r_\alpha \right) / \theta = (r - \sum \rho_\alpha \mathbf{b}_\alpha \cdot \mathbf{u}_\alpha) / \theta .$$

In the mixture conservation laws Truesdell (1984) introduced the field, \mathbf{C}_α , which here is called the *chemical potential tensor* and defined by,

$$\mathbf{C}_\alpha = -\mathbf{T}_\alpha + \rho_\alpha(\varepsilon_\alpha - \theta\eta_\alpha + \frac{1}{2}u_\alpha^2)\mathbf{1} = -\mathbf{T}_\alpha + \rho_\alpha(\psi_\alpha + \frac{1}{2}u_\alpha^2)\mathbf{1} ,$$

where, $\psi_\alpha = \varepsilon_\alpha - \theta\eta_\alpha$, denoting the constituent's *Helmholtz free energy density*, is introduced. Bowen (1984) on the other hand, introduce the *non-kinetic chemical potential tensor*, \mathbf{K}_α , defined by,

$$\rho_\alpha \mathbf{K}_\alpha^T = \mathbf{C}_\alpha - \rho_\alpha \frac{1}{2} u_\alpha^2 \mathbf{1} = \rho_\alpha \psi_\alpha \mathbf{1} - \mathbf{T}_\alpha .$$

Compared to the theory of a single component body there clearly are differences in the relations above for a multi-component formulation. In the definitions of the mixture variables there are contributions from diffusion velocities in addition to sums of the corresponding constituent variables for the stress, internal energy, energy flux, and energy supply. If studying the conservation laws for the mixture it can be seen that the constituent stress tensor are generally allowed to be asymmetric, $\mathbf{T}_\alpha \neq \mathbf{T}_\alpha^T$, and that relations between fluxes and sources of energy and entropy are different compared with a single component formulation. In the multi-component formulation, $\Phi \neq \mathbf{q}/\theta$ and $\sigma \neq r/\theta$, thus, the third of the metaphysical principles of Truesdell is not strictly fulfilled.

5 Chemical potentials

In this section, the for mixtures fundamental concept of *chemical potentials* μ_α , also known as the *partial Gibbs free energy*, is discussed and introduced in the framework we study. The discovery of the concept of chemical potentials for constituents in thermodynamically based theories of mixtures was one of the great achievements of Josiah Willard Gibbs which he reported in “On the equilibrium of heterogeneous substances” published in, 1876 (part 1) and 1878 (part 2).

The nature of the chemical potential is very similar to that of temperature (Müller, 2007). While temperature measures how hot a body is, the chemical potential for a constituent measures how much of that constituent that is present in a body. Also, both measurements are made from outside of the body, by contact. One may also understand this quantity as the energy gained to a mixture when adding a small amount of mass of one of its constituents while keeping entropy and volume constant.

Gibbs obtained his *phase rule* through consideration of the properties of chemical potentials under thermodynamic equilibrium. It states that, under thermodynamic equilibrium, a body with spatially separated phases, p , being mixtures of constituents, the chemical potential, μ_α , for a constituent, α , has equal value for all phases, i.e.

$$\mu_\alpha^p = \mu_\alpha^{Np} \quad \alpha = 1 \dots N\alpha - 1, \quad p = 1 \dots Np - 1,$$

where $N\alpha$ denotes the number of constituents and Np the number of phases. We may use this relation to theoretically construct a membrane permeable for constituent α only, i.e. a semi-permeable membrane. The mixture containing α is considered situated on one side of the membrane (+) and the singular α -material on the other side (-).

$$\mu_\alpha^+ = \mu_\alpha^- \Leftrightarrow \llbracket \mu_\alpha \rrbracket = 0$$

What we obtain is a definition of the chemical potential of constituent α , i.e. the chemical potential μ_α of constituent α may be identified with the quantity that is continuous across a membrane only permeable for α .

In a thermomechanical continuum multi-component framework, an ideal semi-permeable wall, separating a mixture from one of its constituents, α , may be considered in line with what Liu and Müller (1984, chapter 5B.3) describe for their material model proposal. They make use of jump conditions of the balance laws of mass, energy, and entropy, setting the singular surface velocity equal to the mixture velocity v , and ends up with the expression,

$$\llbracket -\theta\Lambda^{\rho\alpha} + \frac{1}{2}(v_\alpha - v)^2 \rrbracket = 0.$$

According to the chemical potential definition given above, now also including non-equilibrium states,

$$\mu_\alpha = \mu_\alpha^I + \frac{1}{2}u_\alpha^2 = -\theta\Lambda^{\rho\alpha} + \frac{1}{2}u_\alpha^2,$$

, where $\mu_\alpha^I = -\theta\Lambda^{\rho\alpha}$ is the “non-kinetic” part of the chemical potential. $-\theta\Lambda^{\rho\alpha}$ may be identified from *Gibbs-Duhem equation*,

$$\sum p_\beta = \sum \rho_\beta (-\theta\Lambda^{\rho\beta}) + \rho(\theta\eta - \varepsilon^I) = \sum \rho_\beta \mu_\beta^I + \rho(\theta\eta - \varepsilon^I),$$

where

$$\varepsilon^I = \sum \frac{\rho_\alpha}{\rho} \varepsilon_\alpha.$$

Gibbs-Duhem in the form above was obtained by Liu and Müller when considering the entropy inequality together with their constitutive relations. Using Gibbs-Duhem for the pure α -constituent side gives,

$$\mu_\alpha = \mu_\alpha^I + \frac{1}{2}u_\alpha^2 = \left(\varepsilon_\alpha - \theta\eta_\alpha + \frac{p_\alpha}{\rho_\alpha} \right) + \frac{1}{2}u_\alpha^2.$$

As can be seen, this expression, when multiplied with the constituent density and the unit tensor, equals the expression defining \mathbf{C}_α given above, the chemical potential tensor, for the case when perfect fluids, for which $\mathbf{T}_\alpha = -p_\alpha \mathbf{1}$ where p_α is the *partial pressure* of constituent α , are considered. From this also the non-kinetic chemical potential tensor, \mathbf{K}_α , is obtained if the last, “kinetic”, term is disregarded. This indicate the motif of the proposed names for \mathbf{K}_α and \mathbf{C}_α .

To gain some additional understanding of the contribution of the chemical potential, it can be instructive to take the point of view of Gurtin (1971), where the *heat flux*, \mathbf{q}' , is taken as the field which divided by temperature gives the entropy flux, i.e. $\mathbf{q}' = \theta\Phi$. Consequently the total energy flux, \mathbf{q} , is given by the sum of the heat flux,

$$\mathbf{q}' = \sum \mathbf{q}_\alpha + \theta \sum \rho_\alpha \eta_\alpha \mathbf{u}_\alpha,$$

and the *diffusive energy flux*,

$$\mathbf{j} = \sum \mathbf{C}_\alpha^T \mathbf{u}_\alpha.$$

Thus, if considering a case of perfect fluids,

$$\mathbf{j} = \sum \rho_\alpha \mu_\alpha \mathbf{u}_\alpha,$$

which indicates that the chemical potential μ_α may be considered a field describing *specific diffusive energy* for constituent α .

5.1 Charged constituents

If constituent α is charged, i.e. has a valence not equal to zero, $z_\alpha \neq 0$, the electrical potential field Φ may have an significant impact on thermomechanical processes.

The framework described above may be generalized as to include the electrical potential field, and as a consequence, yet a term will be added to the chemical potentials (or electrochemical potentials as they also are called in their generalized form). If again identifying the total chemical potential with μ_α and the non-electric part of the chemical potential with $\mu_\alpha^{non-electrical}$, we obtain,

$$\mu_\alpha = \mu_\alpha^{non-electrical} + z_\alpha F \Phi ,$$

where F denote the Faraday constant.

The most general case would be if the electrical potential field is heterogeneous within the body without restrictions, but for our applications it is probably enough to consider heterogeneities in the electrical potential over material interfaces only, e.g. between compacted clay and the deposition hole rock wall. Thus, $\Phi(x, t)$ may suffer a jump at the interface such that,

$$[[\Phi]] = \Phi^+ - \Phi^- .$$

The jump in electrical potential $[[\Phi]]$ is called *membrane* or *Donnan potential*. We may utilize Gibbs phase rule to consider materials on different sides of a semi-permeable membrane,

$$[[\mu_\alpha]] = 0 \Leftrightarrow [[\mu_\alpha^{non-electrical}]] = -z_\alpha F [[\Phi]] ,$$

and obtain what is called *Donnan equilibrium*. As we can see, when charged constituents are introduced in a body with a prescribed piecewise homogeneous electrical potential field, where the homogeneities spatially correspond to the materials within the body, the non-electric part of the chemical potential will suffer jumps at material interfaces. The magnitude of the jump will be dependent on the constituent valence and the jump in electrical potential field between materials.

6 Miscible and immiscible formulations

In the general theoretical framework described in the previous chapter no assumptions has been made regarding the local constitution of the mixture. This naturally results in a description without a local material structure, where the constituents of the mixture blend perfectly, i.e. the mixture is *miscible*. For some mixtures such description is not appropriate, the constituents do not blend and therefore the material obtain a local structure. The mixture is then said to be *immiscible* and the local structure is represented by introducing *volume fractions*, φ_p , of the immiscible *phases*,

$$\varphi_p = dv_p/dv ,$$

where dv_p denote the volume element for phase p in the mixture volume element dv . With the introduction of volume fractions *true mass densities*, γ_p , can be defined by,

$$\varphi_p \gamma_p = \rho_p , \text{ where } \gamma_p = dm_p/dv_p .$$

When introducing the volume fractions these must be added to the dependent variables. Adopting a structure of the material may be seen as constraining the material internally. For the case we are looking at, a scalar, the volume fraction, is introduced to each material point within the body. The volume fraction has to obey certain rules, which will act as constraints of the material. To my knowledge, this is the lowest order of material structure which can be adopted, a single scalar assigned to each material point. In more general theories, sets of scalars or variable vectors may be introduced for describing the structure at material points.

A pragmatic way how to identify the most suitable representation of a specific physical mixture (miscible or immiscible) could be to adopt a definition used by Bowen (1984) when separating classes of models:

“ ... a mixture is immiscible if volume fractions effect the response.”

, i.e. if the concept of volume fractions is needed for describing the material behavior accurately, the mixture is considered immiscible. Another more indirect way would be to take into consideration the material structure on a local scale:

“An immiscible mixture is one where locally one can distinguish between mixture volumes and constituent volumes.”

Bowen (2010)

“These mixtures ... are immiscible, that is, their constituents remain physically separate on a scale which is large in comparison with molecular dimensions.”

Bedford and Drumheller (1983)

Immiscibility has traditionally been used when representing general soil systems by adopting the phases; *solid*, *liquid*, and *gas*, where each phase may consist of several miscible constituents, e.g. dry air and water vapor are miscible and are constituents of the gaseous

phase. Generalizations of classical poromechanical theories may be obtained using immiscibility within the mixture theory framework; see Bowen (1976, 1984, and 2010) for some examples.

7 General constitutive laws for a multi-component body

A miscible thermomechanical process, obeying the laws of conservation, is given by the set of functions corresponding to that of a single component body:

$$\mathbf{v}_\alpha(\mathbf{x}, t), \theta(\mathbf{x}, t), \rho_\alpha(\mathbf{x}, t), \mathbf{T}_\alpha(\mathbf{x}, t), \psi_\alpha(\mathbf{x}, t), \mathbf{q}_\alpha(\mathbf{x}, t), \eta_\alpha(\mathbf{x}, t), \mathbf{b}_\alpha(\mathbf{x}, t) \text{ and } r_\alpha(\mathbf{x}, t),$$

and in addition, the functions,

$$m_\alpha^+(\mathbf{x}, t), \mathbf{m}_\alpha^+(\mathbf{x}, t), \mathbf{M}_\alpha^+(\mathbf{x}, t), e_\alpha^+(\mathbf{x}, t), \text{ and } \gamma_\alpha^+(\mathbf{x}, t),$$

expressing the exchange between constituents. Following and generalizing the procedure as described in the case of single component body,

$$\mathbf{v}_\alpha(\mathbf{x}, t) \text{ and } \theta(\mathbf{x}, t),$$

can be selected to be our independent variables and

$$\mathbf{T}_\alpha(\mathbf{x}, t), \psi_\alpha(\mathbf{x}, t), \mathbf{q}_\alpha(\mathbf{x}, t), \eta_\alpha(\mathbf{x}, t), m_\alpha^+(\mathbf{x}, t), \mathbf{m}_\alpha^+(\mathbf{x}, t), \text{ and } e_\alpha^+(\mathbf{x}, t),$$

as the dependent variables. This may again formally be written using a response function f ,

$$(\mathbf{T}_\alpha(\mathbf{x}, t), \psi_\alpha(\mathbf{x}, t), \mathbf{q}_\alpha(\mathbf{x}, t), \eta_\alpha(\mathbf{x}, t), m_\alpha^+(\mathbf{x}, t), \mathbf{m}_\alpha^+(\mathbf{x}, t), e_\alpha^+(\mathbf{x}, t)) = f(\mathbf{v}_\beta(\cdot, \cdot), \theta(\cdot, \cdot)).$$

An admissible thermomechanical process is a thermodynamic process which is consistent with the response function.

It could be mentioned that since general possibilities for exchanges of mass among the constituents of a mixture are included in the framework described above, expressed by,

$$\sum m_\alpha^+ = 0,$$

representation of chemical reactions is prepared for. More information about this can be found in (Truesdell, 1984), where also works of Bowen, Coleman and Gurtin are mentioned.

8 An immiscible material model with pore pressure

To gain some insight and knowledge about the foundation of “engineering” formulations within soil mechanics, we now study an immiscible formulation within the more general mixture theory framework. The material model chosen is one of Bowen (1984, sect. 5A.4), where $N - 1$ incompressible fluids penetrate an incompressible porous solid. We here, as an example, choose the number of constituents to be three, $N = 3$. The first being the porous solid, the second we denote as gas, and the third liquid.

It should be noted that an assumption of incompressibility for a real gas is probably not a very good choice. Also, it is worth to mention that there are objections to the model studied here (Wilmanski, 2011). Since the model only will be used as an object for studies and comparisons with “engineering” formulations, however, this is not anything that will affect us.

In the model the constitutive assumptions are as follows. The true mass densities, γ_p , are constants, *Helmholtz free energies per mixture volume*, $\Psi_p = \rho_p \psi_p$, are chosen as,

$$\Psi_p = \tilde{\Psi}_p(\theta, \mathbf{F}_s, \varphi_\alpha),$$

and the remaining response function is given by,

$$(\eta_p, \mathbf{m}_p^+ - \lambda \text{grad} \varphi_p, \mathbf{K}_p - \lambda(\varphi_p / \rho_p) \mathbf{1}, \mathbf{M}_p^+, \mathbf{q}) = f(\theta, \text{grad} \theta, \mathbf{F}_s, \text{GRAD} \mathbf{F}_s, \varphi_\alpha, \text{grad} \varphi_\alpha, \mathbf{v}_s, \mathbf{v}_q),$$

where, $p = 1 \dots N$, $q = 2 \dots N$, and $\alpha = 2 \dots N - 1$.

The presence of the scalar multiplier λ comes from indeterminacy in the entropy inequality. This indeterminacy stems from the assumption of incompressibility and this is manifested through the use of λ in \mathbf{m}_p^+ and \mathbf{K}_p . The same conclusion regarding indeterminacy related to incompressibility was also obtained by Alcoverro (2003) when using micro-thermomechanical considerations based on the theory of constrained materials (incompressible) and an averaging procedure in order to obtain a formulation on a “macroscopic” scale.

For the case we consider (solid-gas-liquid),

$$\Psi_s = \tilde{\Psi}_s(\theta, \mathbf{F}_s, \varphi_g), \Psi_g = \tilde{\Psi}_g(\theta, \mathbf{F}_s, \varphi_g) \text{ and } \Psi_l = \tilde{\Psi}_l(\theta, \mathbf{F}_s, \varphi_g).$$

To facilitate the notation and bring it to common ground with what is used in soil mechanics, some definitions of new variables are made. The sum $\sum \Psi_p$ defines the *inner part Helmholtz free energies per mixture volume*, $\Psi^1 = \sum \Psi_p$, $n \equiv 1 - \varphi_s$ defines porosity, and $S_l \equiv \varphi_l / n$ liquid saturation.

When using the constraint given by the entropy inequality according to the Coleman and Noll procedure the following are obtained:

$$\rho \eta = - \frac{\partial \Psi^1}{\partial \theta}, \rho_s \mathbf{K}_s = \varphi_s \lambda \mathbf{1} - \mathbf{F}_s \frac{\partial \Psi^1}{\partial \mathbf{F}_s}, \rho_q \mathbf{K}_q = \varphi_q P_q \mathbf{1}, \text{ and } - \mathbf{m} \cdot \frac{\text{grad} \theta}{\theta} - \sum \mathbf{v}_q \cdot \mathbf{f}_q^+ \geq 0,$$

where

$$P_l = \lambda, P_g = \lambda - \frac{\partial \tilde{\Psi}^I(\theta, \mathbf{F}_s, \varphi_g)}{\partial \varphi_g}, \mathbf{m} = \mathbf{q} + \theta \Sigma \frac{\partial \Psi_p}{\partial \theta} \mathbf{u}_p, \text{ and}$$

$$\mathbf{m}_q^+ = P_q \text{grad} \varphi_q - (\mathbf{F}_s^{-1})^T \left(\frac{\partial \Psi_q}{\partial \mathbf{F}_s} \text{GRAD} \mathbf{F}_s \right) - \frac{\partial \Psi_q}{\partial \varphi_g} \text{grad} \varphi_g + \mathbf{f}_q^+.$$

8.1 Pore pressures

As given above, following results,

$$P_l = \lambda \text{ and } P_g = \lambda - \frac{\partial \tilde{\Psi}^I(\theta, \mathbf{F}_s, \varphi_g)}{\partial \varphi_g},$$

were obtained. Thus, the scalar multiplier introduced due to the indeterminacy in the entropy inequality is identified as the liquid *pore pressure*, P_q .

We may relate the pore pressures to the “non-kinetic” chemical potentials using the result,

$$\rho_q \mathbf{K}_q = \varphi_q P_q \mathbf{1},$$

and the definition of the non-kinetic chemical potential tensor for a perfect fluid, where

$$\mathbf{T}_q = -p_q \mathbf{1},$$

$$\mathbf{K}_q = \mu_q^I \mathbf{1} = \left(\psi_q + \frac{p_q}{\rho_q} \right) \mathbf{1}.$$

If combined we obtain,

$$P_l = \gamma_l \mu_l^I = \gamma_l \psi_l + p_l / \varphi_l \text{ and}$$

$$P_g = \gamma_g \mu_g^I = \gamma_g \psi_g + p_g / \varphi_g .$$

Thus, pore pressures relates to chemical potentials, Helmholtz free energy densities, partial pressures, true mass densities (in this model taken as constants) and volume fractions according to the relations above. The above indicate that generally, pore pressures should not be regarded as pressures in a “physical” sense.

The pore pressure relations above are on a format discussed by Alcoverro (2003) where various possibilities for defining “soil mechanics” stress tensors are considered. In (Alcoverro, 2003) it is assumed that, at a microscopic scale, there may exist body forces, $\rho \mathbf{b}_i$, acting between the constituents and that they derive from a potential ϕ , i.e. $\rho \mathbf{b}_i = -\text{div} \phi$. As a consequence, at a macroscopic scale, “soil mechanics” (*SM*) stress tensors may be formulated as,

$${}^{SM}\mathbf{T}_p = (\mathbf{T}_p - \phi_p \mathbf{1})/\phi_p ,$$

where we may identify,

$${}^{SM}\mathbf{T}_q = -P_q \mathbf{1} , \mathbf{T}_q = -p_q \mathbf{1} , \text{ and } \phi_q = \rho_q \psi_q ,$$

from comparing with the expressions above.

8.2 Capillary pressure (suction) and water retention curve

The difference between the fluid pore pressures is,

$$P^{(C)} \equiv P_g - P_l = \gamma_g \mu_g^I - \gamma_l \mu_l^I = -\frac{\partial \tilde{\Psi}^1(\theta, \mathbf{F}_s, \phi_g)}{\partial \phi_g} ,$$

being the definition of *capillary pressure*, $P^{(C)}$, which equals what also is known as *suction*. For clarity, the relation to chemical potentials is also given above, indicating that generally one should view $P^{(C)}$ as a weighted difference in energy potential between the two fluids, rather than a “physical” pressure difference. If using the relation between pore pressure, partial pressure and Helmholtz free energy together with definitions of porosity, $n \equiv 1 - \phi_s$, and liquid saturation, $S_l \equiv \phi_l/n$, capillary pressure can be expressed,

$$P^{(C)} = \frac{1}{n} \left(\frac{1}{(1 - S_l)} p_g - \frac{1}{S_l} p_l \right) + \frac{1}{n} \left(\frac{1}{(1 - S_l)} \rho_g \psi_g - \frac{1}{S_l} \rho_l \psi_l \right) .$$

In the expression, the first term could be denoted a *matric part* and the second an *osmotic part*.

The function,

$$-\frac{\partial \tilde{\Psi}^1(\theta, \mathbf{F}_s, \phi_g)}{\partial \phi_g} ,$$

represents what is commonly called *water retention curve*.² In this particular constitutive setting the retention curve depends on, temperature, solid deformation, and gas volume fraction.

² It should be noted that if we instead choose the three constituents as, the first being the porous solid, the second liquid, and the third gas, we would obtain,

$$P_g = \lambda , P_l = \lambda - \frac{\partial \tilde{\Psi}^1(\theta, \mathbf{F}_s, \phi_l)}{\partial \phi_l} , \text{ and } P^{(C)} = P_g - P_l = \frac{\partial \tilde{\Psi}^1(\theta, \mathbf{F}_s, \phi_l)}{\partial \phi_l} = \frac{\partial \tilde{\Psi}^1(\theta, \mathbf{F}_s, nS_l)}{\partial (nS_l)} .$$

8.3 Phase mass transport

Bowen also obtained the following expression for the liquid linear momentum production after exploring the entropy inequality,

$$\mathbf{m}_p^+ = P_p \text{grad} \varphi_p - (\mathbf{F}_s^{-1})^T \left(\frac{\partial \Psi_p}{\partial \mathbf{F}_s} \text{GRAD} \mathbf{F}_s \right) - \frac{\partial \Psi_p}{\partial \varphi_g} \text{grad} \varphi_g + \mathbf{f}_p^+ .$$

In the forthcoming discussion we will for simplicity drop the second term on the right hand side, i.e. the contribution from the solid deformation.

The first term on the right hand side $P_p \text{grad} \varphi_p$ is called *buoyancy force* due to arguments originating from hydrodynamics to support such contribution to the momentum supplies. There is a formal argument, first put forward by Müller, for incorporating terms including density gradients (Note that $P_p \text{grad} \varphi_p = \mu_p^I \text{grad} \rho_p$ since γ_p is constant in the present model), if not, the resulting theory is inconsistent with classical thermochemistry (e.g. Bowen, 1974, proof sect. 2.3).

The last contributing term \mathbf{f}_p^+ is called *diffusion forces*. This name can be motivated from concluding that, under isothermal conditions, it disappears when the fluid velocities are zero (Bowen, 2010).

For the present model we assume that we may take the diffusion forces dependent on the temperature, the temperature gradient, and the constituent velocities as indicated by the appearance of \mathbf{v}_s and \mathbf{v}_b in the adopted response function f shown earlier³. Thus, we have that,

$$\mathbf{f}_p^+ = \tilde{\mathbf{f}}_p^+(\theta, \text{grad} \theta, \varphi_b, \text{grad} \varphi_b, \mathbf{v}_s, \mathbf{v}_b).$$

As we have seen in a former section, the stress tensor in the fluids can be expressed,

$$\mathbf{T}_p = -\varphi_p P_p \mathbf{1} + \rho_p \psi_p \mathbf{1} .$$

Using the above in the fluids balance of linear momentum, repeated here,

$$m_p^+ \rho_p \mathbf{v}_p = \rho_p \dot{\mathbf{v}}_p + \text{div} \mathbf{T}_p + \rho_p \mathbf{b}_p + \mathbf{m}_p^+ ,$$

and neglecting, inertial force, mass production, and setting $\mathbf{b}_p = \mathbf{g}$ give,

$$\mathbf{0} = -\varphi_p \text{grad} P_p + \rho_p \mathbf{g} + \tilde{\mathbf{f}}_p^+(\theta, \text{grad} \theta, \varphi_b, \text{grad} \varphi_b, \mathbf{v}_s, \mathbf{v}_b) .$$

We may now adopt constitutive equations for the diffusion forces. Beginning with the isothermal part, one choice could be,

³ I have not seen it being proved for this specific model, but for similar and more general, (Bowen, 1976, 2010).

$$\tilde{\mathbf{f}}_p^+(\theta, \text{grad}\theta, \varphi_b, \text{grad}\varphi_b, \mathbf{v}_s, \mathbf{v}_b)|_{\text{isothermal}} = -\xi_{sp}(\mathbf{v}_p - \mathbf{v}_s),$$

where the material coefficient ξ_{sp} is known as the *drag coefficient*. The equations for liquid and gas now become,

$$\mathbf{v}_l - \mathbf{v}_s = -\frac{\rho_l}{\xi_{sl}} \left(\frac{\varphi_l}{\rho_l} \text{grad}P_l - \mathbf{g} \right) \quad \text{and} \quad \mathbf{v}_g - \mathbf{v}_s = -\frac{\rho_g}{\xi_{sg}} \left(\frac{\varphi_g}{\rho_g} \text{grad}P_g - \mathbf{g} \right),$$

respectively, which are on the ‘‘Darcy’s law format’’. So, Darcy’s law is an approximation of the linear momentum for the fluid constituents.

Here I would like to call attention upon, since it might not be evident from the present description, that for isothermal conditions it is in fact chemical potential gradients, rather than gradients of any ‘‘physical’’ pressure, that are the general driving force that appears naturally in this framework⁴. This can be more clearly seen using that,

$$\frac{\varphi_p}{\rho_p} \text{grad}P_p = \text{grad}\mu_p^I$$

for the present model where γ_p is constant. When inserted in the transportation law we obtain,

$$\mathbf{v}_p - \mathbf{v}_s = -\frac{\rho_p}{\xi_{sp}} (\text{grad}\mu_p^I - \mathbf{g}),$$

which shows the true basis of the phase mass transport.

⁴ See (Bowen, 1976, eqn. 2.9.74, 2.9.50, and 2.9.51) for a clearer view on this matter.

9 Diffusive mass transport of constituents

Here we will divert from the constitutive model proposed by Bowen and turn to general diffusive mass transport in miscible mixtures as described by Liu and Müller (1984, sect. 5B.4). The underlying multi-component formulation is however still the same as described above.

Diffusion flux of a constituent α within a miscible mixture may be described as the flux not attributed to the mean flux of the mixture as a whole. The diffusion origin from molecular transfers of α within the mixture and is an irreversible process.

For the present general framework, when considering perfect fluids and miscibility, Liu and Müller (1984, sect. 5B.4) derive an expression and describe that:

“Fick’s law comes out ... as a mutilated form of the balance of partial momenta.”,

which, as we saw in the previous chapter, also was the case for Darcy’s law. The expression is on the format,

$$\mathbf{u}_\alpha = - \sum_{\beta=1}^{N-1} \mathbf{M}^{\alpha\beta} \text{grad} \mu_{\beta N} - \gamma_\alpha \text{grad} \theta + [\textit{acceleration term}],$$

where, $\mu_{\beta N} = \mu_\beta - \mu_N$, is constituent β ’s *relative chemical potential* with respect to constituent N , $\mathbf{M}^{\alpha\beta}$ is the *mobility tensor* for constituent α with respect to constituent β , the second term on the left hand side represents (a part of) thermal diffusion (the Soret effect), and the last term includes effects from acceleration.

If neglecting the acceleration term, the expression is on the same format as described in Landau and Lifshitz (1959) where a binary mixture is considered. They take partial pressure, p_α , temperature, θ , and concentration, $c_\alpha = \rho_\alpha/\rho$, as their independent variables and express the gradient in chemical potential in terms of these,

$$\text{grad} \mu_{\alpha N} = \frac{\partial \mu_{\alpha N}}{\partial p_\alpha} \text{grad} p_\alpha + \frac{\partial \mu_{\alpha N}}{\partial \theta} \text{grad} \theta + \frac{\partial \mu_{\alpha N}}{\partial c_\alpha} \text{grad} c_\alpha,$$

which gives,

$$\mathbf{u}_\alpha = - \sum_{\beta=1}^{N-1} \mathbf{M}^{\alpha\beta} \frac{\partial \mu_{\beta N}}{\partial p_\beta} \text{grad} p_\beta - \left[\sum_{\beta=1}^{N-1} \left(\mathbf{M}^{\alpha\beta} \frac{\partial \mu_{\beta N}}{\partial \theta} \right) + \gamma_\alpha \right] \text{grad} \theta - \sum_{\beta=1}^{N-1} \mathbf{M}^{\alpha\beta} \frac{\partial \mu_{\beta N}}{\partial c_\beta} \text{grad} c_\beta.$$

Thus, partial pressure, temperature, and concentration are driving forces for diffusion transport in the mixture. The last left hand term may be recognized as “classical” concentration driven diffusion as represented by Fick’s law. The second term is thermal diffusion with has contributions from the direct assumption of temperature driven diffusion as well as from the adopted temperature dependence of the chemical potentials. The first term is representing pressure driven diffusion, e.g. significant in a centrifuge, where constituents with different density can be separated due to this effect.

10 Effective stress

In the field of soil mechanics, several proposals of so-called *effective stress* measures, considered to be suitable when describing the mechanical behavior of the porous material, have been presented. Below a number of propositions of effective stress are given for the present model following the framework described by Alcoverro (2003).

The mixture stress is given by,

$$\mathbf{T} = \sum \mathbf{T}_\alpha - \sum \rho_\alpha \mathbf{u}_\alpha \otimes \mathbf{u}_\alpha.$$

In the following we disregard the by diffusion induced part, $\sum \rho_\alpha \mathbf{u}_\alpha \otimes \mathbf{u}_\alpha$, so that $\mathbf{T} = \sum \mathbf{T}_\alpha$. This could be appropriate for the systems we consider since those often produce small diffusion velocities. For the current model the fluid stresses can be expressed by the partial pressure $p_p = -1/3 \text{tr} \mathbf{T}_p$, the pore pressure, P_p , and Helmholtz free energy, ψ_p , so that,

$$\mathbf{T}_p = -p_p \mathbf{1} = -\varphi_p P_p \mathbf{1} + \rho_p \psi_p \mathbf{1},$$

which, together with the definition above of the total stress tensor, give,

$$\mathbf{T} = \mathbf{T}_s - (p_l + p_g) \mathbf{1} = \mathbf{T}_s - (\varphi_l P_l + \varphi_g P_g) \mathbf{1} + (\rho_l \psi_l + \rho_g \psi_g) \mathbf{1}.$$

We may reformulate this expression to define a “soil mechanics” (*SM*) stress tensor by incorporating the terms of the potential as described by Alcoverro (2003),

$${}^{SM}\mathbf{T} \equiv \mathbf{T} - (\rho_l \psi_l + \rho_g \psi_g) \mathbf{1} = \mathbf{T}_s - (p_l + p_g) \mathbf{1} - (\rho_l \psi_l + \rho_g \psi_g) \mathbf{1} = \mathbf{T}_s - (\varphi_l P_l + \varphi_g P_g) \mathbf{1}.$$

Using definitions of porosity, $n \equiv 1 - \varphi_s$, liquid saturation, $S_l \equiv \varphi_l/n$, and capillary pressure, $P^{(C)} \equiv P_g - P_l$, we obtain,

$${}^{SM}\mathbf{T} = \mathbf{T}_s - n S_l P_l \mathbf{1} - n(1 - S_l) P_g \mathbf{1} = \mathbf{T}_s - n(P_g - S_l P^{(C)}) \mathbf{1}.$$

Since constituents are incompressible in the present representation, a superposed pressure keeps the thermomechanical process unaltered (Alcoverro, 2003). From using this, new *SM*-stresses ${}^{SM}\mathbf{T}'$ may be defined, where one choice is,

$${}^{SM}\mathbf{T}' \equiv {}^{SM}\mathbf{T} + n(P_g - S_l P^{(C)}) \mathbf{1} = \mathbf{T}_s,$$

which has strong similarities with the effective stress measure as proposed by Bishop with the so-called effective stress parameter $\chi = n S_l$. The expression is, however, different to Bishop’s proposal due to the scaling of the gas pore pressure with the porosity in the second term. The relation between total stress and solid stress is equal to what Hutter *et. al.* (1999) obtain in their model where $-\varphi_p P_p^{(\text{Hutter})} = -\varphi_p P_p + \rho_p \psi_p$ and therefore ${}^{SM}\mathbf{T} = \mathbf{T}$.

In order to obtain a *SM*-stress in agreement with Bishop’s proposal we may form ${}^{SM}\mathbf{T}'$ such that,

$${}^{SM}\mathbf{T}' \equiv {}^{SM}\mathbf{T} + (P_g - S_l P^{(C)})\mathbf{1} = \mathbf{T}_s + (1 - n)(P_g - S_l P^{(C)})\mathbf{1}.$$

Definitions of new *SM*-stresses for saturated conditions (*sat*), $S_l = 1$, and unsaturated conditions (*unsat*), $S_l < 1$, may be defined according to,

$${}_{sat}^{SM}\mathbf{T}' \equiv {}^{SM}\mathbf{T} + P_l \mathbf{1} = \mathbf{T}_s + (1 - n)P_l \mathbf{1} \quad \text{and}$$

$${}_{unsat}^{SM}\mathbf{T}' \equiv {}^{SM}\mathbf{T} + P_g \mathbf{1} = \mathbf{T}_s + (1 - n)P_g \mathbf{1} + nS_l P^{(C)} \mathbf{1},$$

where ${}_{sat}^{SM}\mathbf{T}'$ and ${}_{unsat}^{SM}\mathbf{T}'$ as defined above are usually referred to as Terzaghi's effective stress and the net stress, respectively.

11 An immiscible material model with compressibility

As a quite general base case to be used in the next chapter, the immiscible compressible formulation of Bowen (1984, sect. 5A.4) is selected. In the material model $N - 1$ fluids penetrate a porous solid (the first of the constituents and indexed s). In the model the constitutive assumptions are that,

$$\Psi_p = \tilde{\Psi}_p(\theta, \mathbf{F}_s, \rho_q, \varphi_q),$$

and the remaining response function is given by,

$$(\eta_p, \mathbf{m}_p^+, \mathbf{K}_p, \mathbf{M}_p^+, \mathbf{q}, \dot{\varphi}_r) = f(\theta, \text{grad}\theta, \mathbf{F}_s, \text{GRAD}\mathbf{F}_s, \rho_q, \text{grad}\rho_q, \varphi_q, \text{grad}\varphi_q, \mathbf{v}_s, \mathbf{v}_q)$$

where, $p = 1 \dots N$ and $q, r = 2 \dots N$, indicate considerable possibilities for dependencies between the constituents. Bowen now takes the two relations above to be consistent with the entropy inequality in the sense of Coleman and Noll, and obtains the following:

$$\rho\eta = -\frac{\partial\Psi^I}{\partial\theta}, \quad \rho_s\mathbf{K}_s = -\mathbf{F}_s \frac{\partial\Psi^I}{\partial\mathbf{F}_s}, \quad \mathbf{K}_q = \mu_q \mathbf{1}, \quad -\mathbf{m} \cdot \frac{\text{grad}\theta}{\theta} - \sum \mathbf{w}_q \cdot \mathbf{f}_q^+ + \sum \sigma_q \omega_q \geq 0$$

where,

$$\mu_q = \frac{\partial\Psi^I}{\partial\rho_q}, \quad \sigma_q = -\frac{\partial\Psi^I}{\partial\varphi_q}, \quad \mathbf{m} = \mathbf{q} + \theta \sum \frac{\partial\Psi_p}{\partial\theta} \mathbf{u}_p,$$

$$\mathbf{f}_q^+ = \mathbf{m}_q^+ - \mu_q \text{grad}\rho_q + \sigma_q \text{grad}\varphi_q + (\mathbf{F}_s^{-1})^T \left(\frac{\partial\Psi_q}{\partial\mathbf{F}_s} \text{GRAD}\mathbf{F}_s \right) + \sum \frac{\partial\Psi_q}{\partial\rho_r} \text{grad}\rho_r + \sum \frac{\partial\Psi_q}{\partial\varphi_r} \text{grad}\varphi_r,$$

$$\dot{\varphi}_q = \omega_q(\theta, \text{grad}\theta, \mathbf{F}_s, \text{GRAD}\mathbf{F}_s, \rho_r, \text{grad}\rho_r, \varphi_r, \text{grad}\varphi_r, \mathbf{v}_s, \mathbf{v}_r),$$

and

$$\mathbf{w}_p = \mathbf{v}_p - \mathbf{v}_s.$$

Above, ω_q should be understood as the functions that give $\dot{\varphi}_q$.

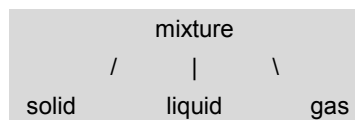
12 Non-associative immiscibility

Here follows a discussion about some ideas of mine regarding how to obtain different levels of immiscibility. I have not seen this particular type of formulation in any of the references, but it seems to strongly relate to double porosity models (e.g. Alcoverro, 2002) and also somewhat to what is called hierarchical or multi-level models, where, fields on a micro-scale are averaged to obtain macro-scale variables. Here however, strictly speaking, scale does not enter the formulation and no averaging is taking place either. Only immiscibility on different levels, generally not connected to scale, is introduced.

If first considering a mixture with phases solid, liquid, and gas and adopting *associative immiscibility* (with an operator denoted (.AI.)), the mixture constitution could formally be expressed as,

$$((\text{solid.AI.liquid}).\text{AI.gas}) = ((\text{gas.AI.solid}).\text{AI.liquid}) = ((\text{liquid.AI.gas}).\text{AI.solid}).$$

Thus, the three mixture constitutions are equal; the order of considering the phases does not matter for associative immiscibility. Another way to express this is to say that the phases are peers on the same level, as indicated in the diagram below.



As a second case we may think of representing a mixture where immiscibility acts on different levels between constituents. This could also be thought of as *non-associative immiscibility*, i.e. the order of which the phases are considered matter. Using non-associative immiscibility (with an operator denoted (.NAI.)) for the same phases as were considered above, would give the three mixture constitutions,

$$((\text{solid.NAI.liquid}).\text{NAI.gas}) \neq ((\text{gas.AI.solid}).\text{NAI.liquid}) \neq ((\text{liquid.NAI.gas}).\text{NAI.solid}),$$

where phases now belong to different levels according to the tree-structures below.



Mixture formulations, denoted *mixture* and *mixture'* are obtained on different levels. It can also be noticed that, for the present case, where both subsequent mixtures have the same number of phases, a recursive structure emerge.

When continuing with discussing the non-associative immiscibility we will select the left case $((\text{solid.NAI.liquid}).\text{NAI.gas})$ since this is a promising candidate for obtaining a representative

model of systems including montmorillonite, water, and air. The solid phase is thought of as containing the minerals, the liquid phase is in itself a miscible mixture of liquid water and dissolved dry air, and the gas phase is also in itself a miscible mixture, of water vapor and dry air, i.e. there are five constituents present in the formulation. For simplicity, however, the three phases are only considered in the following.

In the associative case the solid particles can be considered as surrounded by liquid and gas, but for the chosen non-associative case the solid particles may only be surrounded by the liquid phase, whereas mixture' = (solid.NAI.liquid), consisting of solid particles and the liquid phase, may only be surrounded by gas.

As far as I can understand, the underlying concept of the model proposed above very much resembles that proposed by Alcoverro (2002). The main difference in the concepts is that no "free liquid", which is peer with mixture' and gas in Alcoverro's formulation, is present in the model proposed here.

To see where the concept of non-associative immiscibility will take us I have, tentatively, performed the two step process acquired to formulate the representation of the total mixture using the immiscible compressible formulation of Bowen (1984, sect. 5A.4) reviewed in the former section. For our purposes a single compressible fluid is now considered to penetrate a compressible porous solid, i.e. $N = 2$, in both steps.

The two step formulation process, described in appendix, begins with the lower level mixture', where a solid and the liquid (a fluid) should be considered an immiscible mixture, mixture' = (solid.NAI.liquid). In the next step, mixture', is considered as represented by a porous solid, and yet a fluid (the gas) should be considered as an immiscible mixture which lead to the formulation of the total mixture, mixture = (mixture'.NAI.gas).

When collecting everything in unprimed quantities, thus expressed at the top level, the boxed constitutive relations at the end of this section are obtained.

As can be seen, the scaled liquid volume fraction, φ_l/φ_m , naturally appears in the formulation. If one like, this ratio might be thought of as a lower level ("microscopic") porosity, n' , active on the lower mixture level. For systems containing montmorillonite, the distance between the mineral sheets is a good candidate for partially describing the state of the system at a small scale. The low level porosity, n' , could be thought of as an average representation of the mineral sheet distance.

At the higher mixture level, the gas volume fraction, φ_g , might be seen as a higher level ("macroscopic") porosity, n .

The total porosity, $n_{tot} \equiv 1 - \varphi_s$, is given by,

$$n_{tot} = n'(1 - n) + n,$$

with time derivative,

$$\frac{\dot{n}_{tot}}{1 - n_{tot}} = \frac{\dot{n}'}{1 - n'} + \frac{\dot{n}}{1 - n},$$

which also can be expressed as,

$$\partial_t[\ln(1 - n_{tot})] = \partial_t[\ln(1 - n')] + \partial_t[\ln(1 - n)].$$

$$\varphi_m = 1 - \varphi_g$$

$$\mathbf{v}_m = (\rho_s \mathbf{v}_s + \rho_l \mathbf{v}_l) / (\rho_s + \rho_l)$$

$$\mathbf{F}_m = (\text{grad} \mathbf{v}_m)^{-1} \text{GRAD} \mathbf{v}_m$$

$$\Psi_s = \tilde{\Psi}_s \left(\theta, \mathbf{F}_s, \frac{\varphi_l}{\varphi_m} \gamma_l, \frac{\varphi_l}{\varphi_m}, \rho_g, \varphi_g \right)$$

$$\Psi_l = \tilde{\Psi}_l \left(\theta, \mathbf{F}_s, \frac{\varphi_l}{\varphi_m} \gamma_l, \frac{\varphi_l}{\varphi_m}, \rho_g, \varphi_g \right)$$

$$\Psi_g = \tilde{\Psi}_g(\theta, \mathbf{F}_m, \rho_g, \varphi_g)$$

$$\begin{aligned} & (\varphi_m \eta_s, \mathbf{m}_s^+, \mathbf{K}_s, \mathbf{M}_s^+) \\ & = f_s \left(\theta, \text{grad} \theta, \mathbf{F}_s, \text{GRAD} \mathbf{F}_s, \frac{\varphi_l}{\varphi_m} \gamma_l, \text{grad} \left(\frac{\varphi_l}{\varphi_m} \gamma_l \right), \frac{\varphi_l}{\varphi_m}, \text{grad} \frac{\varphi_l}{\varphi_m}, \rho_g, \text{grad} \rho_g, \varphi_g, \text{grad} \varphi_g, \mathbf{v}_s, \mathbf{v}_l, \mathbf{v}_g \right) \end{aligned}$$

$$\begin{aligned} & \left(\varphi_m \eta_l, \mathbf{m}_l^+, \mathbf{K}_l, \mathbf{M}_l^+, \partial_t \left(\frac{\varphi_l}{\varphi_m} \right) \right) \\ & = f_l \left(\theta, \text{grad} \theta, \mathbf{F}_s, \text{GRAD} \mathbf{F}_s, \frac{\varphi_l}{\varphi_m} \gamma_l, \text{grad} \left(\frac{\varphi_l}{\varphi_m} \gamma_l \right), \frac{\varphi_l}{\varphi_m}, \text{grad} \frac{\varphi_l}{\varphi_m}, \rho_g, \text{grad} \rho_g, \varphi_g, \text{grad} \varphi_g, \mathbf{v}_s, \mathbf{v}_l, \mathbf{v}_g \right) \end{aligned}$$

$$(\eta_g, \mathbf{m}_g^+, \mathbf{K}_g, \mathbf{M}_g^+, \dot{\varphi}_g) = f_g(\theta, \text{grad} \theta, \mathbf{F}_m, \text{GRAD} \mathbf{F}_m, \rho_g, \text{grad} \rho_g, \varphi_g, \text{grad} \varphi_g, \mathbf{v}_m, \mathbf{v}_g)$$

$$\mathbf{q}_m = \tilde{\mathbf{q}}_m \left(\theta, \text{grad} \theta, \mathbf{F}_s, \text{GRAD} \mathbf{F}_s, \frac{\varphi_l}{\varphi_m} \gamma_l, \text{grad} \left(\frac{\varphi_l}{\varphi_m} \gamma_l \right), \frac{\varphi_l}{\varphi_m}, \text{grad} \frac{\varphi_l}{\varphi_m}, \mathbf{v}_s, \mathbf{v}_l \right)$$

$$\mathbf{q} = \mathbf{q}_m + \tilde{\mathbf{q}}(\theta, \text{grad} \theta, \mathbf{F}_m, \text{GRAD} \mathbf{F}_m, \rho_g, \text{grad} \rho_g, \varphi_g, \text{grad} \varphi_g, \mathbf{v}_m, \mathbf{v}_g)$$

13 Summary and concluding remarks

I have found it very enlightening when conducting this literature study. Many assumptions upon which the “engineering” formulations we rely on rests became visible to me for the first time. This kind of study also gives a possibility to discover parts where there could be potential for future developments.

Here follows a list with some selected conclusions.

- The chemical potential is a fundamental part of both classical and modern mixture theories.
- To allow for general and mechanism-based models, jump conditions, i.e. discontinuities in fields, should be possible.
- Miscible and immiscible formulations are possible. Immiscibility leads to adopting a material structure represented by volume fractions. Porosity and degree of saturation may be defined in terms of volume fractions.
- Pore pressures for fluid phases are generally not “physical” pressures, they are scaled chemical potentials.
- Thereby, “Capillary pressure”, or suction, is the difference between scaled chemical potentials.
- Darcy’s law and Fick’s law are obtained from simplifying linear momentum of the phase or constituent, respectively. Chemical potential and temperature are the basic driving forces.

My own modest contribution is a concept of non-associative immiscibility which gives a mixture with immiscibility on different levels. An attempt to schematically formulate a material model using this concept has been described, and in this formulation, porosities belonging to the different levels are obtained.

Studies of general theoretical frameworks and existing valid constitutive relations in “modern” mixture theory (it has been around since the late sixties) very much enhance the understanding of our current tools based on “engineering” formulations. A deeper understanding of the foundation on which our present numerical tools rest could hardly be a disadvantage. Also, I believe that studies of general frameworks may give indications of directions where to search for potential for progress concerning our current formulations.

In this study I have mostly been looking at the foundations of mixture theory as described in references belonging to a period rather early in its development. To get a picture of the current “state of the art” in this field one would probably have to study more recent references, e.g. (Müller and Ruggeri, 1993), (Hutter et al., 1999), (Wilmanski; 2005, 2011), and (Jussila, 2007).

For facilitating deeper understanding and testing the theories, it seems suitable to formulate simple problems that could be solved using general mathematical tools, for instance MathCad or Comsol Multiphysics. Such implementations could also serve as a tool for evaluating what is gained as compared to existing models.

The incorporation of chemical reactions has not been addressed here, mostly so since it certainly is not my field of expertise. The framework does, however, incorporate such possibilities in its core. As far as I understand, no ad hoc additions are needed when performing the incorporation of chemistry into the framework. I have seen several references to literature where incorporation of chemical reactions is described, so my impression is that this is quite established.

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15 References

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16 Appendix

Following the concept of non-associative immiscibility outlined above, for mixture' = (solid.NAI.liquid) we obtain:

$$\varphi'_s = dv_s/dv' , \varphi'_l = dv_l/dv' ,$$

$$\rho'_s = dm_s/dv' , \rho'_l = dm_l/dv' ,$$

$$\rho'_m = \rho'_s + \rho'_l : \text{total mass density for mixture' ,}$$

$$\mathbf{v}'_m = 1/\rho'_m(\rho'_s \mathbf{v}_s + \rho'_l \mathbf{v}_l) : \text{barycentric velocities for mixture' ,}$$

$$\mathbf{u}'_s = \mathbf{v}_s - \mathbf{v}'_m , \mathbf{u}'_l = \mathbf{v}_l - \mathbf{v}'_m ,$$

$$\varphi'_p \gamma_p = \rho'_p , \text{ where } \gamma_p = dm_p/dv_p .$$

and the constitutive laws:

$$\Psi'_s = \tilde{\Psi}'_s(\theta, \mathbf{F}_s, \rho'_l, \varphi'_l),$$

$$\Psi'_l = \tilde{\Psi}'_l(\theta, \mathbf{F}_s, \rho'_l, \varphi'_l),$$

$$(\eta'_s, \mathbf{m}_s^+, \mathbf{K}_s, \mathbf{M}_s^+) = f'_s(\theta, \text{grad}\theta, \mathbf{F}_s, \text{GRAD}\mathbf{F}_s, \rho'_l, \text{grad}\rho'_l, \varphi'_l, \text{grad}\varphi'_l, \mathbf{v}_s, \mathbf{v}_l),$$

$$(\eta'_l, \mathbf{m}_l^+, \mathbf{K}_l, \mathbf{M}_l^+, \dot{\varphi}'_l) = f'_l(\theta, \text{grad}\theta, \mathbf{F}_s, \text{GRAD}\mathbf{F}_s, \rho'_l, \text{grad}\rho'_l, \varphi'_l, \text{grad}\varphi'_l, \mathbf{v}_s, \mathbf{v}_l), \text{ and}$$

$$\mathbf{q}'_m = \tilde{\mathbf{q}}'_m(\theta, \text{grad}\theta, \mathbf{F}_s, \text{GRAD}\mathbf{F}_s, \rho'_l, \text{grad}\rho'_l, \varphi'_l, \text{grad}\varphi'_l, \mathbf{v}_s, \mathbf{v}_l).$$

For mixture = (mixture'.NAI.gas) we obtain:

$$\varphi_m = dv'/dv, \varphi_g = dv_g/dv,$$

$$\rho_m = dm_m/dv, \rho_g = dm_g/dv,$$

$$\rho = \rho_m + \rho_g : \text{total mass density for mixture,}$$

$$\mathbf{v} = 1/\rho(\rho_m \mathbf{v}_m + \rho_g \mathbf{v}_g): \text{barycentric velocities for mixture,}$$

$$\mathbf{u}_m = \mathbf{v}_m - \mathbf{v}, \mathbf{u}_g = \mathbf{v}_g - \mathbf{v}, \text{ and}$$

$$\varphi_p \gamma_p = \rho_p, \text{ where } \gamma_p = dm_p/dv_p,$$

with the constitutive relations,

$$\Psi_m = \tilde{\Psi}_m(\theta, \mathbf{F}_m, \rho_g, \varphi_g),$$

$$\Psi_g = \tilde{\Psi}_g(\theta, \mathbf{F}_m, \rho_g, \varphi_g),$$

$$(\eta_m, \mathbf{m}_m^+, \mathbf{K}_m, \mathbf{M}_m^+) = f_m(\theta, \text{grad}\theta, \mathbf{F}_m, \text{GRAD}\mathbf{F}_m, \rho_g, \text{grad}\rho_g, \varphi_g, \text{grad}\varphi_g, \mathbf{v}_m, \mathbf{v}_g),$$

$$(\eta_g, \mathbf{m}_g^+, \mathbf{K}_g, \mathbf{M}_g^+, \phi_g) = f_g(\theta, \text{grad}\theta, \mathbf{F}_m, \text{GRAD}\mathbf{F}_m, \rho_g, \text{grad}\rho_g, \varphi_g, \text{grad}\varphi_g, \mathbf{v}_m, \mathbf{v}_g), \text{ and}$$

$$\mathbf{q} = \tilde{\mathbf{q}}(\theta, \text{grad}\theta, \mathbf{F}_m, \text{GRAD}\mathbf{F}_m, \rho_g, \text{grad}\rho_g, \varphi_g, \text{grad}\varphi_g, \mathbf{v}_m, \mathbf{v}_g).$$

The two mixture models at different levels above might be “tied together” by expressing primed quantities, with reference volume = dv' , in terms of unprimed quantities, with reference volume = dv . The following is obtained:

$$\varphi_m = 1 - \varphi_g,$$

$$\varphi_s = \varphi_m \varphi'_s, \varphi_l = \varphi_m \varphi'_l,$$

$$\rho_s = \varphi_m \rho'_s, \rho_l = \varphi_m \rho'_l, \rho_m = \varphi_m \rho'_m = \varphi_m \rho'_s + \varphi_m \rho'_l = \rho_s + \rho_l,$$

$$\mathbf{v}_m = \mathbf{v}'_m = (\rho'_s \mathbf{v}_s + \rho'_l \mathbf{v}_l)/\rho'_m = (\rho_s \mathbf{v}_s + \rho_l \mathbf{v}_l)/\rho_m,$$

$$\mathbf{u}_s = \mathbf{u}'_s, \mathbf{u}_l = \mathbf{u}'_l,$$

$$\Psi'_s = \rho'_s \psi'_s = \frac{\rho_s}{\varphi_m} \psi'_s = \rho_s \psi_s = \Psi_s, \Psi'_l = \rho'_l \psi'_l = \frac{\rho_l}{\varphi_m} \psi'_l = \rho_l \psi_l = \Psi_l,$$

$$\rho'_s \eta'_s = \frac{\rho_s}{\varphi_m} \eta'_s = \rho_s \eta_s, \rho'_l \eta'_l = \frac{\rho_l}{\varphi_m} \eta'_l = \rho_l \eta_l,$$

$$\rho = \rho_m + \rho_g = \rho_s + \rho_l + \rho_g,$$

$$\mathbf{v} = 1/\rho(\rho_s \mathbf{v}_s + \rho_l \mathbf{v}_l + \rho_g \mathbf{v}_g),$$

$$\mathbf{u}_m = \mathbf{v}_m - \mathbf{v} = (\rho_s \mathbf{v}_s + \rho_l \mathbf{v}_l)/\rho_m - (\rho_s \mathbf{v}_s + \rho_l \mathbf{v}_l + \rho_g \mathbf{v}_g)/\rho, \mathbf{u}_g = \mathbf{v}_g - \mathbf{v}, \text{ and}$$

$$\mathbf{F}_m = \mathbf{L}_m^{-1} \dot{\mathbf{F}}_m, \dot{\mathbf{F}}_m = \partial \mathbf{v}_m / \partial \mathbf{X}_m = \text{GRAD} \mathbf{v}_m, \mathbf{L}_m = \partial \mathbf{v}_m / \partial \mathbf{x}_m = \text{grad} \mathbf{v}_m.$$

When collecting everything in unprimed quantities following constitutive relations are obtained:

$$\varphi_m = 1 - \varphi_g$$

$$\mathbf{v}_m = (\rho_s \mathbf{v}_s + \rho_l \mathbf{v}_l) / (\rho_s + \rho_l)$$

$$\mathbf{F}_m = (\text{grad} \mathbf{v}_m)^{-1} \text{GRAD} \mathbf{v}_m$$

$$\Psi_s = \tilde{\Psi}_s \left(\theta, \mathbf{F}_s, \frac{\varphi_l}{\varphi_m} \gamma_l, \frac{\varphi_l}{\varphi_m}, \rho_g, \varphi_g \right)$$

$$\Psi_l = \tilde{\Psi}_l \left(\theta, \mathbf{F}_s, \frac{\varphi_l}{\varphi_m} \gamma_l, \frac{\varphi_l}{\varphi_m}, \rho_g, \varphi_g \right)$$

$$\Psi_g = \tilde{\Psi}_g(\theta, \mathbf{F}_m, \rho_g, \varphi_g)$$

$$\begin{aligned} & (\varphi_m \eta_s, \mathbf{m}_s^+, \mathbf{K}_s, \mathbf{M}_s^+) \\ & = f_s \left(\theta, \text{grad} \theta, \mathbf{F}_s, \text{GRAD} \mathbf{F}_s, \frac{\varphi_l}{\varphi_m} \gamma_l, \text{grad} \left(\frac{\varphi_l}{\varphi_m} \gamma_l \right), \frac{\varphi_l}{\varphi_m}, \text{grad} \frac{\varphi_l}{\varphi_m}, \rho_g, \text{grad} \rho_g, \varphi_g, \text{grad} \varphi_g, \mathbf{v}_s, \mathbf{v}_l, \mathbf{v}_g \right) \end{aligned}$$

$$\begin{aligned} & \left(\varphi_m \eta_l, \mathbf{m}_l^+, \mathbf{K}_l, \mathbf{M}_l^+, \partial_t \left(\frac{\varphi_l}{\varphi_m} \right) \right) \\ & = f_l \left(\theta, \text{grad} \theta, \mathbf{F}_s, \text{GRAD} \mathbf{F}_s, \frac{\varphi_l}{\varphi_m} \gamma_l, \text{grad} \left(\frac{\varphi_l}{\varphi_m} \gamma_l \right), \frac{\varphi_l}{\varphi_m}, \text{grad} \frac{\varphi_l}{\varphi_m}, \rho_g, \text{grad} \rho_g, \varphi_g, \text{grad} \varphi_g, \mathbf{v}_s, \mathbf{v}_l, \mathbf{v}_g \right) \end{aligned}$$

$$(\eta_g, \mathbf{m}_g^+, \mathbf{K}_g, \mathbf{M}_g^+, \dot{\varphi}_g) = f_g(\theta, \text{grad} \theta, \mathbf{F}_m, \text{GRAD} \mathbf{F}_m, \rho_g, \text{grad} \rho_g, \varphi_g, \text{grad} \varphi_g, \mathbf{v}_m, \mathbf{v}_g)$$

$$\mathbf{q}_m = \tilde{\mathbf{q}}_m \left(\theta, \text{grad} \theta, \mathbf{F}_s, \text{GRAD} \mathbf{F}_s, \frac{\varphi_l}{\varphi_m} \gamma_l, \text{grad} \left(\frac{\varphi_l}{\varphi_m} \gamma_l \right), \frac{\varphi_l}{\varphi_m}, \text{grad} \frac{\varphi_l}{\varphi_m}, \mathbf{v}_s, \mathbf{v}_l \right)$$

$$\mathbf{q} = \mathbf{q}_m + \tilde{\mathbf{q}}(\theta, \text{grad} \theta, \mathbf{F}_m, \text{GRAD} \mathbf{F}_m, \rho_g, \text{grad} \rho_g, \varphi_g, \text{grad} \varphi_g, \mathbf{v}_m, \mathbf{v}_g)$$