

Macroscopic Modeling of Porous Materials

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1 Introduction

Macroscopic modeling of porous bodies is a task which cannot be solved universally for all materials possibly belonging to this class. Porous bodies are aggregates of solid elements (grains, various matrices) and whose voids form the pore space. In order to construct continuum macroscopic models this microscopic heterogeneity has to be smeared out by some homogenization technique. Even the purpose of this smearing transition is still not properly understood by some researchers. For instance, within soil mechanics, models are often using the notion of the so-called real (true) mass density of components, $\rho^{\alpha R}$ (α is labeling the component; e.g. $\alpha = S$ for the solid component, $\alpha = F$ for the fluid, or $\alpha = G$ for the gaseous component). This mass density is identical with the mass density of the component when considered alone outside of the porous medium (e.g. $\rho^{FR} = 1000$ kg/m³ for water under normal conditions). These mass densities are well-defined in porous bodies only in those points where a particular component indeed appears. In order to construct a continuum model, one has to extend the domain of definition on a domain, say $\mathcal{B}_0 \subset \mathfrak{R}^3$, common for all components. This means that either one has to make an arbitrary extension of the true density on parts of the domain where a chosen component does not appear or one has to smear out this quantity which yields a definition of the so-called partial densities, characteristic for a macroscopic continuum theory of mixtures. In our simple homogeneous example of water saturating a porous medium whose voids cover, say, 25% of the total volume such a mass density would be $\rho^F = 0.25 \cdot \rho^{FR} = 250$ kg/m³. It is the first procedure for which it is often advocated within soil mechanics. The second procedure was systematically introduced by C. Truesdell [1] for the so-called miscible mixtures of fluids. Most likely, G. Heinrich and K. Desoyer [2,3] were the first authors who used the mixture theory for porous media. Such mixtures are called immiscible (e.g. R. A. Bowen [4]).

In addition, as always in the case of smearing it is necessary to close such a procedure with some *ad hoc* relations (the closure problem) which may vary from one model to the other. The best known and investigated are problems of transition from a microscopic description to the so-called thermodynamic region within the kinetic theory of gases (see: Chapter 7 in [5]).

For porous materials, the most commonly used homogenization technique is the volume averaging over the so-called representative elementary volume (*REV*). These domains must be large enough to enable the averaging and small enough to apply a continuum model. Unfortunately, these properties of *REV* cannot be made mathematically precise.

As indicated by T. Bourbie, O. Coussy, B. Zinszner [6] the domain REV may be dependent on the quantity which we define.

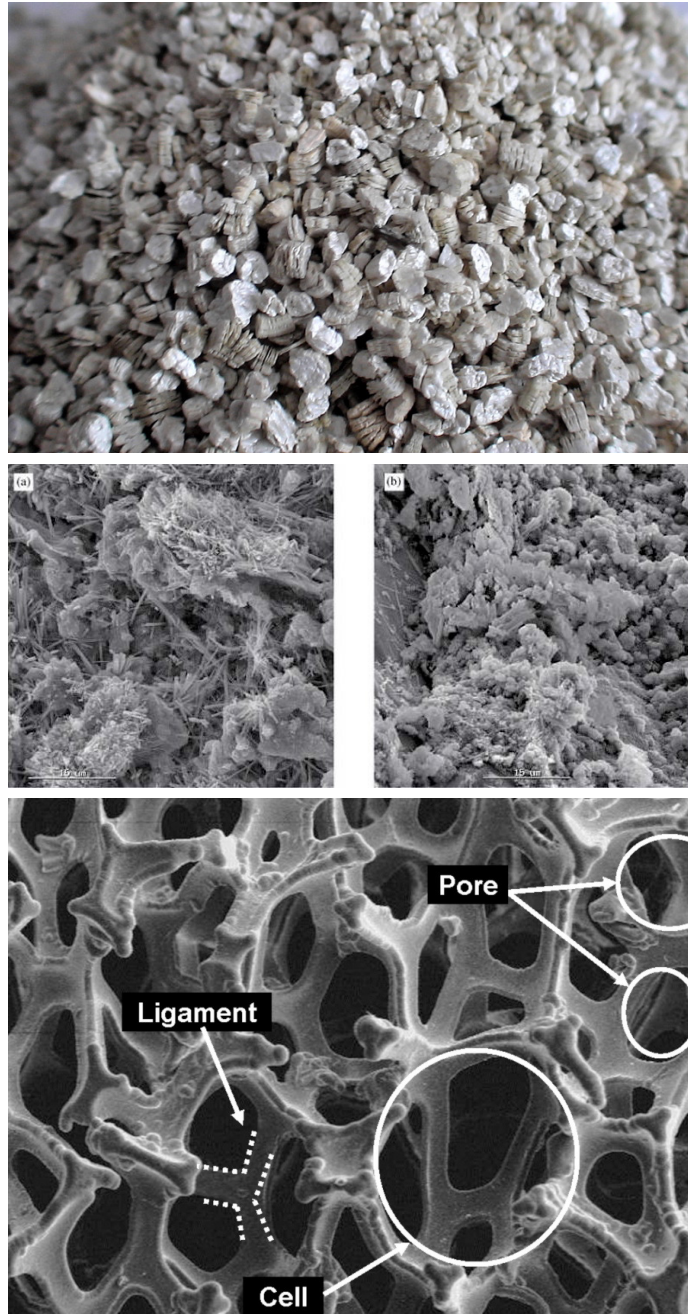


Fig.1 : *Examples of microstructure for various porous materials*

- 1) upper panel: loose granular material (exfoliated vermiculite, porosity app. 0.4),
- 2) middle panel: concrete (a/ region of formation of ettringite, b/ portlandite and calcium silicates, porosity app. 0.1),
- 3) lower panel: foam (porosity app. 0.9).

For instance, the porosity of a porous material is defined by the relation

$$n(\mathbf{X}, t) = 1 - \frac{1}{\text{vol}(REV)} \int_{REV(\mathbf{x}, t)} \chi^S(\mathbf{Z}, t) dV_z, \quad (1)$$

where $REV(\mathbf{X}, t)$ is the domain of the real porous medium ascribed to a point $\mathbf{X} \in \mathcal{B}_0$ of the continuum at the instant of time t , $\chi^S(\mathbf{Z}, t)$, $\mathbf{Z} \in REV(\mathbf{X}, t)$ is the characteristic function for the solid component, i.e. it is one when the point \mathbf{Z} is occupied by the solid at the instant of time t and zero otherwise. $\text{vol}(REV)$ denotes the volume of $REV(\mathbf{X}, t)$. Clearly, such a definition is characteristic for the description of a body with microstructure. The average (1) may not be adequate, for instance, for the quantity called the degree of saturation which is, in turn, the volume fraction of the liquid to the joint volume of liquid and gas. Namely, in the case of very low degree of saturation, very few bubbles of the gas are spread in large volumes of the liquid which means that, in contrast to porosity, one needs much larger domains for an appropriate average of saturation. A similar remark concerns the convection properties of the medium which is characterized by the permeability coefficient (e.g. [7]). It is even worse that these properties may vary strongly in time and in space. Consequently, a construction of averages by means of representative elementary volumes should be taken with a pinch of salt. J. Bear [8] demonstrates an example of applicability of the notion of porosity as an average. This is shown in Fig.2. If the domain of REV is too small there are large fluctuations of porosity depending on the position in space in which the average is calculated. For inhomogeneous media in which porosity changes from place to place there is also an influence of the size chosen too large in which some layers, for instance, will not be seen.

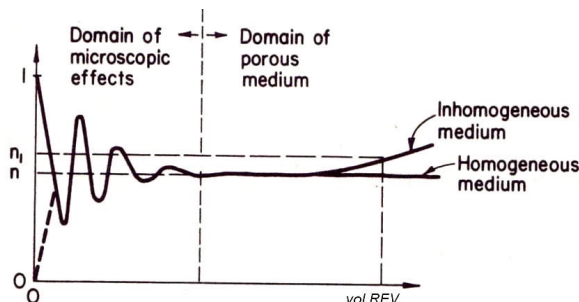


Fig. 2: Definition of porosity in dependence on the size of REV [8]

An additional problem appears when the medium is cracked. This is, for instance, the case in many geotechnical applications to rocks. Then the size of REV sufficient for a usual porosity may be much too small for cracks. In such media one has to introduce very often a so-called double porosity (e.g. [9]).

Unfortunately, these remarks do not exhaust problems with averaging techniques for porous media. In the case of such materials as composites or polycrystals (considered as aggregates of monocrystalline grains) one can most likely improve procedures so far that macroscopic properties of materials (elastic parameters, viscoplastic properties, etc.) follow with a sufficient accuracy for their practical applicability (compare the classical works of E. Kröner [10] and Z. Hashin and S. Shtrikman [11]). This is not the case for aggregates in which the diffusion appears. It means that porous and, in particular, granular materials in which a fluid in pores moves with a different kinematics than the solid skeleton, require not only special averaging techniques but also some image analysis of the microstructure (e.g. see: [12]) in order to sort out properties which mostly influence the relative motion. Apart from permeability this may be, for instance, the tortuosity, i.e.

some measure of local curvatures of microchannels. For instance, by inspection of the lower panel of Fig.1 it is easy to imagine that a macroscopic one-dimensional homogeneous flow of a fluid through a foam corresponds to wild variations of momentum, both in magnitude and direction, on the real material. It is still a very much open question how to account for such "fluctuations" in macroscopic model and no averaging procedure gave any reasonable hint for the solution of this problem.

These few remarks on the microstructural properties of porous media seem to justify a purely phenomenological continuum approach extended more or less intuitively by a set of microstructural variables. Certainly, one should try to justify such macroscopic models by relations to microstructure as far as possible in the present state of research but a hope for a full derivation of macroscopic equations by some homogenization procedure does not seem to be justified.

In this work, we present some fundamental properties of macroscopic modeling of the so-called thermoelastic porous materials which admit large deformations of the solid skeleton. For the lack of space we shall make only occasional and very brief references to the microscopic interpretations and motivations of the model. We begin with the presentation of a general theory of the Lagrangian description of kinematics and balance equations for porous materials, as well as a small remark on a thermodynamic strategy of construction of models. Then we discuss a few constitutive properties of thermoporoelastic materials. We complete this presentation with equations of a linear model introduced by Biot which is fundamental for poroacoustics. At the end of the work we make a few comments on linear modeling of unsaturated media.

2 Kinematics and balance equations in Lagrangian description

It is well known in classical continuum mechanics that the description of motion is usually performed in two different ways. The Eulerian description is characteristic for fluids and it operates on families of subdomains of the configuration space (the space of motion) which are usually chosen to be time independent (i.e. they contain the same points of the configuration space). Then a material flows through such domains with the kinematics given by a field of velocity $\mathbf{v}(\mathbf{x}, t)$, $\mathbf{x} \in \mathcal{B} \subset \mathcal{R}^3$. Balance laws in this description must account for fluxes through boundaries of subdomains. The Lagrangian description is characteristic for solids and it operates on subdomains \mathcal{P} in a reference configuration $\mathcal{B}_0 \subset \mathcal{R}^3$ which are also time independent. These subdomains contain always the same material particles $\mathbf{X} \in \mathcal{B}_0$ which is, of course, not the case for subdomains of Eulerian description. The kinematics is given by the so-called function of motion $\mathbf{x} = \mathbf{f}(\mathbf{X}, t)$ which describes the current position \mathbf{x} of the particle \mathbf{X} in the configuration space. Its partial time derivative defines the field of velocity. In linear models the function of motion is usually defined by the displacement vector \mathbf{u} . We do not use this notion in this work.

Porous materials consists of both solid skeleton and fluid components in pores. Consequently, one can choose either Eulerian description which would emphasize the motion of the fluid component or Lagrangian description which would emphasize the motion of the skeleton. The first approach is convenient, for instance, in the description of suspensions. The second approach is appropriate for a (physically) compact skeleton appearing

in rocks, foams, ceramics and granular materials sustained by a confining pressure (e.g. soils). We use this second description.

For a multicomponent immiscible mixture which consists of a solid skeleton and A fluid components in pores the motion of the skeleton is assumed to be described by the function of motion

$$\mathbf{x} = \mathbf{f}^S(\mathbf{X}, t), \quad \mathbf{X} \in \mathcal{B}_0, \quad (2)$$

whose first derivatives define the deformation gradient and the velocity, respectively,

$$\mathbf{F}^S(\mathbf{X}, t) = \text{Grad } \mathbf{f}^S, \quad \dot{\mathbf{x}}^S(\mathbf{X}, t) = \frac{\partial \mathbf{f}^S}{\partial t}. \quad (3)$$

When necessary, we use Cartesian frames in which the above objects have the following components

$$\mathbf{F}^S = F_{kK}^S \mathbf{e}_k \otimes \mathbf{e}_K, \quad \dot{\mathbf{x}}^S = \dot{x}_k^S \mathbf{e}_k, \quad (4)$$

where $\{\mathbf{e}_k\}_{k=1}^3$ are unit orthogonal vectors of the Eulerian coordinates and $\{\mathbf{e}_K\}_{K=1}^3$ are unit orthogonal vectors of the Lagrangian coordinates. Metric tensors of both systems are, obviously, Kronecker deltas: $\delta_{kl} = \mathbf{e}_k \cdot \mathbf{e}_l$, $\delta_{KL} = \mathbf{e}_K \cdot \mathbf{e}_L$. The deformation gradient of the skeleton for the reference configuration is chosen to be represented by the unit matrix: $\mathbf{F}^S = \mathbf{1}$. The possibility of this description has been indicated by O. Coussy [13] and it was systematically introduced to porous models by K. Wilmanski (e.g. [14, 15]). Let us mention in passing that there are papers on this subject in which the Lagrangian description is introduced separately for each component. It is not only an unnecessary formal complication but sometimes it yields erroneous results.

The aim of the model is to find the following fields defined in points \mathbf{X} of the reference domain $\mathcal{B}_0 \subset \mathfrak{R}^3$ and in instances t of the time interval $\mathcal{T} \subset [0, \infty)$:

1. partial mass density of the skeleton referred to a unit reference volume: $\rho^S(\mathbf{X}, t)$,
2. partial mass densities of the fluid components referred to a unit reference volume: $\rho^\alpha(\mathbf{X}, t)$, $\alpha = 1, \dots, A$,
3. velocity of the skeleton: $\dot{\mathbf{x}}^S(\mathbf{X}, t)$,
4. deformation gradient of the skeleton: $\mathbf{F}^S(\mathbf{X}, t)$, $J^S := \det \mathbf{F}^S > 0$,
5. velocities of fluid components $\dot{\mathbf{x}}^\alpha(\mathbf{X}, t)$, $\alpha = 1, \dots, A$,
6. porosity: $n(\mathbf{X}, t)$,
7. temperature common for all components $T(\mathbf{X}, t)$.

Consequently a thermomechanical process is described by the mapping

$$\mathbf{w} : (\mathbf{X}, t) \mapsto \mathfrak{R}^{4A+15}, \quad \mathbf{w} := \{\rho^S, \rho^\alpha, \dot{\mathbf{x}}^S, \mathbf{F}^S, \dot{\mathbf{x}}^\alpha, n, T\}, \quad \alpha = 1, \dots, A. \quad (5)$$

Field equations for these fields follow from balance equations which we proceed to formulate.

Balance equations are specified in their global form on material domains of components. For porous materials in the Lagrangian description the family of material domains

for the skeleton satisfies conditions identical with those of the classical continuum mechanics. As already mentioned, material domains of the skeleton are time independent because the reference configuration \mathcal{B}_0 is defined with respect to the deformation gradient of skeleton \mathbf{F}^S . For this configuration $\mathbf{F}^S = \mathbf{1}$.

It is not the case any more for fluid components. They have different kinematics than the skeleton which means that domains in the space of motion containing during the motion the same particles of a particular fluid component move with respect to material domains of the skeleton. In the Eulerian description the velocity field for this motion is given by the difference $\mathbf{v}^\alpha(\mathbf{x}, t) - \mathbf{v}^S(\mathbf{x}, t)$ for the fluid component α , where $\mathbf{v}^\alpha(\mathbf{x}, t)$ is the velocity of the fluid and $\mathbf{v}^S(\mathbf{x}, t)$ is the velocity of the skeleton at the same spatial position \mathbf{x} and at the same instant of time t . This relative motion yields the time dependence of material domains of fluid components projected on the reference configuration \mathcal{B}_0 . The projection is carried by the function of motion of the skeleton (2), whose existence is assumed in the model. The condition for the existence of the function of motion \mathbf{f}^S shall be formulated later.

In order to describe the kinematics of material fluid domains projected on the reference configuration we consider the mappings shown in Fig. 3. In the current configuration $\mathcal{B}_t = \mathbf{f}^S(\mathcal{B}_0, t)$ we consider an arbitrary subset $\mathcal{P}_t^\alpha \subset \mathcal{B}_t$ which is material with respect to the component α , i.e. by an infinitesimal increment of time, Δt , it becomes $\mathcal{P}_{t+\Delta t}^\alpha := \{\mathbf{x} \in \mathcal{B}_{t+\Delta t} \mid \mathbf{x} - \mathbf{v}^\alpha(\mathbf{x}, t + \Delta t) \Delta t \in \mathcal{P}_t^\alpha\}$. These two subsets of the space of current configurations are maps of the subsets $\mathcal{P}^\alpha(t), \mathcal{P}^\alpha(t + \Delta t)$ of the reference configuration \mathcal{B}_0 , one at the instant of time t and the other at the instant of time $t + \Delta t$. Obviously, they contain the same particles of the component α . This construction is shown in Fig. 3. Now, we choose an arbitrary particle of the component α which occupies the position $\mathbf{x} \in \mathcal{P}_t^\alpha$ at the instant of time t , i.e. its position in the reference configuration is $\mathbf{X} = \mathbf{f}^{S^{-1}}(\mathbf{x}, t)$. Its position $\mathbf{x} + \Delta \mathbf{x}$ at the instant $t + \Delta t$ can be written in the form

$$\begin{aligned} \mathbf{x} + \Delta \mathbf{x} &= \mathbf{x} + \dot{\mathbf{x}}^\alpha(\mathbf{X}, t) \Delta t = \mathbf{f}^S(\mathbf{X} + \Delta \mathbf{X}, t + \Delta t) = \\ &= \mathbf{x} + \text{Grad } \mathbf{f}^S(\mathbf{X}, t) \Delta \mathbf{X} + \frac{\partial \mathbf{f}^S}{\partial t} \Delta t = \\ &= \mathbf{x} + \mathbf{F}^S \Delta \mathbf{X} + \dot{\mathbf{x}}^S \Delta t. \end{aligned} \quad (6)$$

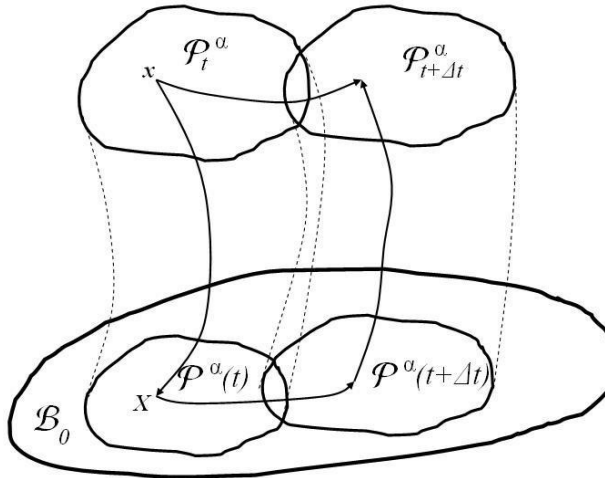


Fig. 3: Reference configuration for immiscible mixtures

Consequently, the set $\mathcal{P}^\alpha(t) \subset \mathcal{B}_0$ is endowed with the kinematics defined by the following velocity field

$$\forall \mathbf{X} \in \mathcal{B}_0 : \quad \lim_{\Delta t \rightarrow 0} \frac{\Delta \mathbf{X}}{\Delta t} = \dot{\mathbf{X}}^\alpha(\mathbf{X}, t) = \mathbf{F}^{S-1}(\dot{\mathbf{x}}^\alpha - \dot{\mathbf{x}}^S). \quad (7)$$

Obviously, in the above relations we were using the following transformations

$$\dot{\mathbf{x}}^S(\mathbf{X}, t) = \mathbf{v}^S(\mathbf{f}^S(\mathbf{X}, t), t), \quad \dot{\mathbf{x}}^\alpha(\mathbf{X}, t) = \mathbf{v}^\alpha(\mathbf{f}^S(\mathbf{X}, t), t). \quad (8)$$

The fields $\dot{\mathbf{X}}^\alpha$ are called Lagrangian velocity fields of fluid components. The index α may be also equal to S as $\dot{\mathbf{X}}^S \equiv \mathbf{0}$.

As indicated above the Lagrangian description exposes the role of material subdomains of components. In order to appreciate the operational meaning of the transformation of velocities to the Lagrangian description, we formulate balance equations of mass for all components. They have the following form

$$\frac{d}{dt} \int_{\mathcal{P}^S} \rho^S dV = \int_{\mathcal{P}^S} \hat{\rho}^S dV, \quad (9)$$

for every material domain of the skeleton $\mathcal{P}^S \subset \mathcal{B}_0$, and

$$\frac{d}{dt} \int_{\mathcal{P}^\alpha(t)} \rho^\alpha dV = \int_{\mathcal{P}^\alpha(t)} \hat{\rho}^\alpha dV, \quad (10)$$

for every material domain of the α fluid component $\mathcal{P}^\alpha(t) \subset \mathcal{B}_0$, $\alpha = 1, \dots, A$. In the above relations $\hat{\rho}^S, \hat{\rho}^\alpha$ are the mass sources which satisfy the following bulk conservation law

$$\forall \mathbf{X} \in \mathcal{B}_0, t \in \mathcal{T} : \quad \hat{\rho}^S + \sum_{\alpha=1}^A \hat{\rho}^\alpha = 0. \quad (11)$$

Time dependence of material domains for fluid components yields the following rules of time differentiation

$$\begin{aligned} \frac{d}{dt} \int_{\mathcal{P}^S} \rho^S dV &= \int_{\mathcal{P}^S} \frac{\partial}{\partial t} \rho^S dV, \\ \frac{d}{dt} \int_{\mathcal{P}^\alpha(t)} \rho^\alpha dV &= \int_{\mathcal{P}^\alpha(t)} \frac{\partial}{\partial t} \rho^\alpha dV + \oint_{\partial \mathcal{P}^\alpha(t)} \rho^\alpha \mathbf{N} \cdot \dot{\mathbf{X}}^\alpha dS, \end{aligned} \quad (12)$$

where \mathbf{N} denotes the unit normal vector field of the boundary $\partial \mathcal{P}^\alpha(t)$.

These relations yield the following local form of mass balance equations for $\alpha = 1, \dots, A$,

$$\frac{\partial \rho^S}{\partial t} = \hat{\rho}^S, \quad \frac{\partial \rho^\alpha}{\partial t} + \text{Div}(\rho^\alpha \dot{\mathbf{X}}^\alpha) = \hat{\rho}^\alpha, \quad (13)$$

in regular points (almost everywhere) of \mathcal{B}_0 , and

$$U [[\rho^S]] = 0, \quad \left[\left[\rho^\alpha (\dot{\mathbf{X}}^\alpha \cdot \mathbf{N} - U) \right] \right] = 0, \quad (14)$$

in points of singular surfaces moving through the reference configuration \mathcal{B}_0 with the local speed U . The brackets $[[\dots]]$ denote the difference of finite limits of quantities in these brackets on the positive and negative side of the surface.

It is seen in the above relations that the Lagrangian velocities $\dot{\mathbf{X}}^\alpha$ replace in this description the velocities \mathbf{v}^α of the Eulerian description.

In a similar manner we obtain the following partial momentum balance equations in their local form. For the regular points of the reference configuration \mathcal{B}_0

$$\begin{aligned} \frac{\partial (\rho^S \dot{\mathbf{x}}^S)}{\partial t} - \text{Div } \mathbf{P}^S &= \hat{\mathbf{p}}^S + \rho^S \mathbf{b}^S, \\ \frac{\partial (\rho^\alpha \dot{\mathbf{x}}^\alpha)}{\partial t} + \text{Div} \left(\rho^\alpha \dot{\mathbf{x}}^\alpha \otimes \dot{\mathbf{X}}^\alpha - \mathbf{P}^\alpha \right) &= \hat{\mathbf{p}}^\alpha + \rho^\alpha \mathbf{b}^\alpha, \quad \hat{\mathbf{p}}^S + \sum_{\alpha=1}^A \hat{\mathbf{p}}^\alpha = 0, \end{aligned} \quad (15)$$

and for points on singular surfaces

$$\begin{aligned} \rho^S U [[\dot{\mathbf{x}}^S]] + [[\mathbf{P}^S]] \mathbf{N} &= 0, \\ \rho^\alpha \left(\dot{\mathbf{X}}^\alpha \cdot \mathbf{N} - U \right) [[\dot{\mathbf{x}}^\alpha]] - [[\mathbf{P}^\alpha]] \mathbf{N} &= 0. \end{aligned} \quad (16)$$

In these relations $\mathbf{P}^S, \mathbf{P}^\alpha$ denote partial Piola-Kirchhoff stress tensors, $\mathbf{b}^S, \mathbf{b}^\alpha$ are partial mass forces, and $\hat{\mathbf{p}}^S, \hat{\mathbf{p}}^\alpha$ denote the momentum sources. Relation (15)₃ expresses the bulk conservation of momentum.

We do not need to present details of partial energy balance equations. Under the assumption of a single field of temperature we need solely the bulk energy conservation law. The derivation is based on a principle of the theory of mixtures formulated by C. Truesdell that bulk quantities must be defined in such a way that balance equations for these quantities have the form of classical conservation laws of the single component continuum thermodynamics.

Bearing this principle in mind we define the following bulk quantities

$$\rho = \rho^S + \sum_{\alpha=1}^A \rho^\alpha, \quad \rho \dot{\mathbf{x}} = \rho^S \dot{\mathbf{x}}^S + \sum_{\alpha=1}^A \rho^\alpha \dot{\mathbf{x}}^\alpha, \quad \rho \dot{\mathbf{X}} = \sum_{\alpha=1}^A \rho^\alpha \dot{\mathbf{X}}^\alpha, \quad (17)$$

which are the bulk mass density, the bulk momentum, and an objective relative momentum connected with the reference of the motion to the skeleton rather than to local centers of gravity for mixtures of fluids in Eulerian description;

$$\begin{aligned} \mathbf{P} &= \mathbf{P}_I - \mathbf{F}^S \left\{ \rho^S \dot{\mathbf{X}} \otimes \dot{\mathbf{X}} + \sum_{\alpha=1}^A \rho^\alpha \left(\dot{\mathbf{X}}^\alpha - \dot{\mathbf{X}} \right) \otimes \left(\dot{\mathbf{X}}^\alpha - \dot{\mathbf{X}} \right) \right\}, \\ \mathbf{P}_I &= \mathbf{P}^S + \sum_{\alpha=1}^A \mathbf{P}^\alpha; \end{aligned} \quad (18)$$

this is the bulk Piola-Kirchhoff stress tensor with the so-called intrinsic part \mathbf{P}_I ;

$$\begin{aligned} \rho \varepsilon &= \rho \varepsilon_I + \frac{1}{2} \left\{ \rho^S \mathbf{C}^S \cdot \left(\dot{\mathbf{X}} \otimes \dot{\mathbf{X}} \right) + \sum_{\alpha=1}^A \rho^\alpha \mathbf{C}^S \cdot \left(\dot{\mathbf{X}}^\alpha - \dot{\mathbf{X}} \right) \otimes \left(\dot{\mathbf{X}}^\alpha - \dot{\mathbf{X}} \right) \right\}, \\ \rho \varepsilon_I &= \rho^S \varepsilon^S + \sum_{\alpha=1}^A \rho^\alpha \varepsilon^\alpha, \quad \mathbf{C}^S = \mathbf{F}^{ST} \mathbf{F}^S, \end{aligned} \quad (19)$$

this is the bulk specific internal energy with the intrinsic part $\rho\varepsilon_I$. The symmetric tensor \mathbf{C}^S is the right Cauchy-Green deformation tensor of the skeleton;

$$\begin{aligned}\mathbf{Q} &= \mathbf{Q}_I + \frac{1}{2} \left\{ -\rho^S \dot{\mathbf{X}} \otimes \dot{\mathbf{X}} \otimes \dot{\mathbf{X}} + \right. \\ &\quad \left. + \sum_{\alpha=1}^A \rho^\alpha (\dot{\mathbf{X}}^\alpha - \dot{\mathbf{X}}) \otimes (\dot{\mathbf{X}}^\alpha - \dot{\mathbf{X}}) \otimes (\dot{\mathbf{X}}^\alpha - \dot{\mathbf{X}}) \right\} \mathbf{C}^S, \\ \mathbf{Q}_I &= \mathbf{Q}^S + \sum_{\alpha=1}^A \mathbf{Q}^\alpha - \rho^S \varepsilon^S \dot{\mathbf{X}} + \sum_{\alpha=1}^A \rho^\alpha \varepsilon^\alpha (\dot{\mathbf{X}}^\alpha - \dot{\mathbf{X}}) + \\ &\quad + \mathbf{P}^{ST} \mathbf{F}^S \dot{\mathbf{X}} - \sum_{\alpha=1}^A \mathbf{P}^{\alpha T} \mathbf{F}^S (\dot{\mathbf{X}}^\alpha - \dot{\mathbf{X}}),\end{aligned}\tag{20}$$

and this vector describes the bulk heat flux in the Lagrangian description. Again the intrinsic part \mathbf{Q}_I was separated.

The bulk balance equation of energy can now be written in the following form

$$\frac{\partial}{\partial t} \rho \left(\varepsilon + \frac{1}{2} \dot{x}^2 \right) + \text{Div} \left\{ \rho \left(\varepsilon + \frac{1}{2} \dot{x}^2 \right) \dot{\mathbf{X}} + \mathbf{Q} - \mathbf{P}^T \dot{\mathbf{x}} \right\} = \rho \mathbf{b} \cdot \dot{\mathbf{x}} + \rho r,\tag{21}$$

where

$$\begin{aligned}\rho \mathbf{b} &= \rho^S \mathbf{b}^S + \sum_{\alpha=1}^A \rho^\alpha \mathbf{b}^\alpha, \\ \rho r &= \rho^S r^S + \sum_{\alpha=1}^A \rho^\alpha r^\alpha - \rho^S \mathbf{b}^S \cdot \mathbf{F}^S \dot{\mathbf{X}} + \sum_{\alpha=1}^A \rho^\alpha \mathbf{b}^\alpha \cdot \mathbf{F}^S (\dot{\mathbf{X}}^\alpha - \dot{\mathbf{X}}),\end{aligned}\tag{22}$$

and r^S, r^α denote the partial radiations.

In the Lagrangian description and with the choice of fields (5) we have at disposal the following integrability condition

$$\frac{\partial \mathbf{F}^S}{\partial t} = \text{Grad } \dot{\mathbf{x}}^S.\tag{23}$$

This condition yields the existence of the function of motion (2). By the choice (5) of unknown fields this relation plays the role of the field equation for the deformation gradient \mathbf{F}^S .

It is useful to write equation (23) in the following weaker form

$$\frac{d}{dt} \int_{\mathcal{P}^S} \mathbf{F}^S dV = \oint_{\partial \mathcal{P}^S} \dot{\mathbf{x}}^S \otimes \mathbf{N} dS,\tag{24}$$

for every material domain of the skeleton $\mathcal{P}^S \subset \mathcal{B}_0$. This balance equation yields the following condition in points of singular surfaces

$$U [[\mathbf{F}^S]] = - [[\dot{\mathbf{x}}^S]] \otimes \mathbf{N}.\tag{25}$$

This relation is usually derived by means of the Hadamard Theorem for singular surfaces.

Before we present remaining equations of the model let us discuss some properties of the objects which we have introduced above. It is easy to notice a striking similarity of the structure of bulk quantities to that appearing in the classical theory of mixtures. This concerns terms with explicit contributions of velocities. However in contrast to the mixture theory all velocities of the present model are objective because $\dot{\mathbf{X}}^\alpha$ and $\dot{\mathbf{X}}$ are relative velocities. Due to constitutive relations these velocities may be also present in the implicit form in intrinsic parts of stress tensors, internal energy and heat flux vector. It is also important to notice that the explicit dependence is at least quadratic. If we consider processes with small deviations from the thermodynamical equilibrium these contributions can be neglected.

In order to turn over mass balance equations (5), momentum balance equations (15), energy balance equation (21) and compatibility condition (23) into field equations for fields (5) we need constitutive relations for partial stress tensors, momentum sources, the bulk internal energy and the bulk heat flux. If we had these relations we would have $14(A + 1)$ equations. Consequently we would be missing one equation. This is connected with the fact that the porosity n is the additional microstructural variable and this requires an additional equation. We proceed to formulate this equation.

There are various ways in which one can describe changes of porosity. One can assume that it is given by a constitutive equation of the same nature as stresses or the internal energy. In linear models it is often assumed that these changes are proportional to changes of the volume of the skeleton. Such a proposition was made by Gassmann [16]. Another constitutive relation follows within the linear Biot model in which also volume changes of the fluid have an influence on porosity. A second order differential equation describing changes of porosity was proposed by Goodman and Cowin [17] in their model of combustion of granular materials. This equation has been modified and still serves as one of the most popular approaches to this problem. In description of plastic deformations of soils it is sometimes assumed that the true mass density of the skeleton does not change (incompressibility) and this yields an equation for porosity changes. Since some 15 years there exists also a proposition to describe porosity changes by a balance equation [18, 19]. This equation has the form

$$\frac{\partial \Delta_n}{\partial t} + \text{Div } \mathbf{J} = \hat{n}, \quad \Delta_n = n - n_E, \quad (26)$$

where Δ_n is the deviation of porosity from the equilibrium value n_E , the latter together with the flux of porosity \mathbf{J} and the source of porosity \hat{n} must be given by constitutive relations. We expect that n tends to an equilibrium under constant external conditions. The equilibrium value of porosity n_E satisfies the equation (26) with the flux and source equal to zero. The latter as we show later follow indeed from the second law of thermodynamics. It can be shown that the above equation yields as particular cases linear models of Gassmann and Biot. In contrast to other propositions the above equation is appropriate for arbitrary deformations of the skeleton. Simultaneously, it contains a source term which accounts for changes of porosity due to microcracking in, for instance, freezing and melting, or other nonisochoric phase changes and for natural relaxation processes of biomaterials.

Making an assumption that sources of porosity do not carry surface singularities we

can write the following compatibility condition for porosity on such surfaces

$$U [[\Delta_n]] - [[\mathbf{J}]] \cdot \mathbf{N} = 0, \quad (27)$$

which may suggest the form of natural boundary conditions for porosity.

Let us collect balance equations which we have discussed in this Section. They are shown in the Tables 1 and 2.

Table 1: Balance equations for the $A + 1$ -component porous material in regular points of the reference configuration $\mathbf{X} \in \mathcal{B}_0$

mass of S	$\frac{\partial \rho^S}{\partial t} = \hat{\rho}^S$
mass of α	$\frac{\partial \rho^\alpha}{\partial t} + \text{Div } \rho^\alpha \dot{\mathbf{X}}^\alpha = \hat{\rho}^\alpha$
momentum of S	$\frac{\partial(\rho^S \dot{\mathbf{x}}^S)}{\partial t} - \text{Div } \mathbf{P}^S = \hat{\mathbf{p}}^S + \rho^S \mathbf{b}^S$
momentum of α	$\frac{\partial(\rho^\alpha \dot{\mathbf{x}}^\alpha)}{\partial t} + \text{Div} \left(\rho^\alpha \dot{\mathbf{x}}^\alpha \otimes \dot{\mathbf{X}}^\alpha - \mathbf{P}^\alpha \right) = \hat{\mathbf{p}}^\alpha + \rho^\alpha \mathbf{b}^\alpha$
bulk energy	$\frac{\partial}{\partial t} \rho \left(\varepsilon + \frac{1}{2} \dot{x}^2 \right) + \text{Div} \left\{ \rho \left(\varepsilon + \frac{1}{2} \dot{x}^2 \right) \dot{\mathbf{X}} + \mathbf{Q} - \mathbf{P}^T \dot{\mathbf{x}} \right\} = \rho \mathbf{b} \cdot \dot{\mathbf{x}} + \rho r$
integrability of \mathbf{F}^S	$\frac{\partial \mathbf{F}^S}{\partial t} = \text{Grad } \dot{\mathbf{x}}^S$
porosity	$\frac{\partial \Delta_n}{\partial t} + \text{Div } \mathbf{J} = \hat{n}$

Table 2: Balance equations (dynamic compatibility conditions) in points of the singular surface

mass of S	$U \llbracket \rho^S \rrbracket = 0$
mass of α	$\llbracket \rho^\alpha \left(\dot{\mathbf{X}}^\alpha \cdot \mathbf{N} - U \right) \rrbracket = 0$
momentum of S	$\rho^S U \llbracket \dot{\mathbf{x}}^S \rrbracket + \llbracket \mathbf{P}^S \rrbracket \cdot \mathbf{N} = 0,$
momentum of α	$\rho^\alpha \left(\dot{\mathbf{X}}^\alpha \cdot \mathbf{N} - U \right) \llbracket \dot{\mathbf{x}}^\alpha \rrbracket - \llbracket \mathbf{P}^\alpha \rrbracket \cdot \mathbf{N} = 0$
integrability	$U \llbracket \mathbf{F}^S \rrbracket = - \llbracket \dot{\mathbf{x}}^S \rrbracket \otimes \mathbf{N}$
porosity	$U \llbracket \Delta_n \rrbracket - \llbracket \mathbf{J} \rrbracket \cdot \mathbf{N} = 0$

As already indicated we do not quote here the dynamic compatibility relation for the bulk energy.

In order to construct field equations for the fields \mathbf{w} listed in relation (5) we have to solve the *closure problem*, i.e. we have to add constitutive relations to balance equations of Table 1. We shall do so for some important particular cases.

3 Second law of thermodynamics

In order to be more specific we consider a nonlinear model describing a fully saturated porous material. It means that we consider a two-component immiscible mixture: $\alpha = S$ or $\alpha = F$. We limit the attention to the so-called thermoporoelastic model which must specify the following fundamental fields

$$\mathcal{F} = \{\rho^S, \rho^F, \dot{\mathbf{x}}^S, \dot{\mathbf{x}}^F, \mathbf{F}^S, T, n\}. \quad (28)$$

It means that the model contains only one microstructural variable – porosity, n . However, in an implicit way some additional properties of microstructure are also incorporated in the present model. It has been shown in the work [20] that some microscopic fluctuations of microscopic velocities can be accounted for in the model if we include a nonlinear (at least quadratic) dependence on the relative velocity and a dependence on relative accelerations. The latter must be first properly defined as the difference of the second time derivatives $\partial(\dot{\mathbf{x}}^F - \dot{\mathbf{x}}^S)/\partial t$ is not objective and, consequently, cannot be used as a constitutive variable. It has been shown in the above quoted paper [20] that this definition must be of the following form

$$\mathbf{a}_r \equiv \frac{\partial}{\partial t} (\dot{\mathbf{x}}^F - \dot{\mathbf{x}}^S) - (1 - \mathfrak{z}) \dot{\mathbf{X}}^F \cdot \text{Grad } \dot{\mathbf{x}}^F - \mathfrak{z} \dot{\mathbf{X}}^F \cdot \text{Grad } \dot{\mathbf{x}}^S, \quad (29)$$

where \mathfrak{z} is an arbitrary scalar. There is an obvious similarity of this definition to definitions of objective time derivatives appearing, for instance, in nonlinear plasticity. The object (29) transforms under the time dependent change of observer: $\mathbf{x}^* = \mathbf{O}(t)\mathbf{x}$, where \mathbf{O} is orthogonal $O^T = \mathbf{O}^{-1}$ – it describes the rotation of the reference system, in the following manner

$$\mathbf{a}_r^* = \mathbf{O}\mathbf{a}_r, \quad (30)$$

which means that \mathbf{a}_r is objective.

We return to the interpretation of the above indicated extension of the set of constitutive variables after the discussion of the second law of thermodynamics.

Field equations for the fields (28) which follow from the above presented balance laws must be constructed by means of the closure relations. These are constitutive relations for the constitutive quantities of the model

$$\mathcal{C} = \{\hat{\rho}^S, \mathbf{P}^S, \mathbf{P}^F, \hat{\mathbf{p}}^S, \varepsilon, \mathbf{Q}, \mathbf{J}, \hat{n}\}. \quad (31)$$

They are functions of the following set of constitutive variables

$$\mathcal{R} = \left\{ \rho^S, \rho^F, \mathbf{F}^S, \dot{\mathbf{X}}^F, \Delta_n, T, \mathbf{G}, \mathbf{N}, \mathbf{a}_r \right\}, \quad \mathbf{G} = \text{Grad } T, \quad \mathbf{N} = \text{Grad } n, \quad (32)$$

where the relative acceleration \mathbf{a}_r is defined by the relation (29). The presence of both partial mass densities is necessary only in the case of mass exchange between components. Otherwise, only the mass density ρ^F would appear in order to describe volume changes of the fluid component. Obviously, \mathbf{F}^S accounts for the deformations of the skeleton, $\dot{\mathbf{X}}^F$ for the relative motion of components (diffusion), Δ_n for nonequilibrium changes of porosity, T for nonisothermal character of processes, \mathbf{G} for heat conduction, \mathbf{N} for heterogeneity of porosity, and \mathbf{a}_r for relative acceleration of components. Experience with the derivation of

Biot's model shows that the dependence on \mathbf{N} is essential for the admissibility of certain couplings in a linear model (e.g. [21]).

Constitutive relations

$$\mathcal{C} = \mathcal{C}(\mathcal{R}) \quad (33)$$

contain in addition a parametric dependence on the initial porosity n_0 . In the case of residual partial stresses which may appear in the configuration \mathcal{B}_0 , they should also be present in a parametric way in constitutive relations. It is, for instance the case when the fluid component is the gas or for granular materials which remain compact under confining pressure. Constitutive relations should satisfy a set of principles characteristic for a thermodynamic strategy of constructing continuous models. We shall not present here any details of this strategy referring the reader to monographs on the subject (e.g. [5]). However, in some details we discuss consequences of the second law of thermodynamics. We proceed to formulate this law in the Lagrangian description of two-component porous materials. The case of multicomponent immiscible mixtures was considered in the work [22].

The fundamental assumption of this formulation refers to the existence of partial entropy densities, η^S, η^F , which satisfy balance laws

$$\frac{\partial \rho^S \eta^S}{\partial t} + \text{Div } \mathbf{H}^S = \hat{\eta}^S, \quad (34)$$

$$\frac{\partial \rho^F \eta^F}{\partial t} + \text{Div} \left(\rho^F \eta^F \dot{\mathbf{X}}^F + \mathbf{H}^F \right) = \hat{\eta}^F,$$

in which $\mathbf{H}^S, \mathbf{H}^F$ are partial entropy fluxes, and $\hat{\eta}^S, \hat{\eta}^F$ are partial entropy sources. Addition of these relations yields

$$\frac{\partial \rho \eta}{\partial t} + \text{Div} \left(\rho \eta \dot{\mathbf{X}} + \mathbf{H} \right) = \hat{\eta}^S + \hat{\eta}^F, \quad (35)$$

where

$$\rho \eta = \rho^S \eta^S + \rho^F \eta^F, \quad \mathbf{H} = \mathbf{H}^S + \mathbf{H}^F + \frac{\rho^S \rho^F}{\rho} (\eta^F - \eta^S) \dot{\mathbf{X}}^F. \quad (36)$$

The most essential part of the second law of thermodynamics which we consider in this work is the assumption that the source of entropy $\hat{\eta}^S + \hat{\eta}^F$ is nonnegative for all solutions of field equations. This yields the following entropy inequality

$$\frac{\partial \rho \eta}{\partial t} + \text{Div} \left(\rho \eta \dot{\mathbf{X}} + \mathbf{H} \right) \geq 0, \quad \eta = \eta(\mathcal{R}), \quad \mathbf{H} = \mathbf{H}(\mathcal{R}), \quad (37)$$

which must hold for all admissible processes, i.e. solutions of field equations.

Comparison of relations (20) and (36) reveals that even in the case of classical Fourier relations between partial fluxes $\mathbf{H}^S = \mathbf{Q}^S/T$ and $\mathbf{H}^F = \mathbf{Q}^F/T$, one cannot expect a similar relation to hold for the bulk fluxes \mathbf{Q} and \mathbf{H} . This has been observed by I. Müller for mixtures of fluids and it holds also for porous materials. For immiscible mixtures it is even more obvious as the intrinsic flux \mathbf{Q}_I may be anisotropic with respect to the diffusion due to the contribution of partial stresses (compare (20)) while \mathbf{H} (36) does not possess such a contribution. In a particular case, when, for some reason or other, one can neglect an influence of shear stresses in the relation (20) it follows

$$\mathbf{Q}_I = \mathbf{Q}^S + \mathbf{Q}^F + \frac{\rho^S \rho^F}{\rho} \left(\left(\varepsilon^F + \frac{p^F}{\rho_t^F} \right) - \left(\varepsilon^S + \frac{p^S}{\rho_t^S} \right) \right) \dot{\mathbf{X}}^F, \quad (38)$$

where

$$\begin{aligned} p^S &= -\frac{1}{3}J^{S-1} \operatorname{tr} \mathbf{P}^S \mathbf{F}^{ST}, & p^F &= -\frac{1}{3}J^{S-1} \operatorname{tr} \mathbf{P}^F \mathbf{F}^{ST}, \\ \rho_t^S &= J^{S-1} \rho^S, & \rho_t^F &= J^{S-1} \rho^F, & J^S &= \operatorname{tr} \mathbf{F}^S, \end{aligned} \quad (39)$$

i.e. p^S, p^F are partial pressures, while ρ_t^S, ρ_t^F are current partial mass densities. In such a case, the second part of the intrinsic flux \mathbf{Q}_I is parallel to $\dot{\mathbf{X}}^F$ but the coefficients $(\varepsilon^F + p^F/\rho_t^F) - (\varepsilon^S + p^S/\rho_t^S)$ (difference of specific enthalpies) in \mathbf{Q}_I and $(\eta^F - \eta^S)$ (difference of specific entropies) in \mathbf{H} are not related only by the factor $1/T$. If this were the case then this would mean equal chemical potentials of components (i.e. $(\varepsilon^F + p^F/\rho_t^F - T\eta^F) = (\varepsilon^S + p^S/\rho_t^S - T\eta^S)$) which, of course, does not hold in general. It is one of the properties of the thermodynamic equilibrium.

Even less one can say about different partial temperatures. In such a case not only Fourier relations do not hold but, in addition, some other components of the second law cannot be formulated in a standard way. This concerns particularly continuity conditions on boundaries between different systems and, consequently, a measurability of partial temperatures. It can be easily checked that partial temperatures cannot be continuous through boundaries (e.g. [14]). Some progress has been recently made for mixtures of gases but even there the solution is still not complete [23].

Exploitation of the entropy inequality (37) is based on the elimination of constraints on the space of its solutions by means of Lagrange multipliers (e.g. [5], [15]). In the case of the model under consideration one has to consider the following inequality

$$\begin{aligned} \frac{\partial \rho \eta}{\partial t} + \operatorname{Div} \left(\rho \eta \dot{\mathbf{X}} + \mathbf{H} \right) - \Lambda^{\rho^S} R^S - \Lambda^{\rho^F} R^F - \\ - \Lambda^{v^S} \cdot \mathbf{M}^S - \Lambda^{v^F} \cdot \mathbf{M}^F - \Lambda^\varepsilon E - \Lambda^n D - \Lambda^{FS} \cdot \mathbf{F} \geq 0, \end{aligned} \quad (40)$$

for all fields (28). The multipliers $\Lambda^{\rho^S}, \Lambda^{\rho^F}, \Lambda^{v^S}, \Lambda^{v^F}, \Lambda^\varepsilon, \Lambda^n, \Lambda^{FS}$ are functions of constitutive variables (32). In contrast to the entropy inequality (37), the above inequality must hold for arbitrary fields and not only for solutions of field equations.

4 Simplified constitutive relations

Apart from usual restrictions of material objectivity (i.e. invariance with respect to changes of observers), we assume additionally that the system is isotropic and that a dependence on vectorial constitutive variables $\dot{\mathbf{X}}^F, \mathbf{G}, \mathbf{N}, \mathbf{a}_r$ has the lowest nontrivial order. The same assumption concerns the deviation of porosity from equilibrium, Δ_n . For the purpose of this work we neglect as well the exchange of mass between components $\hat{\rho}^S = 0$. Then the mass density ρ^S does not appear as a constitutive variable and the multiplier $\Lambda^{\rho^S} = 0$.

These assumptions yield the following structure of constitutive relations
– partial stresses

$$\mathbf{P}^S = \mathbf{P}_0^S(\mathcal{R}_E, \Delta_n) + \frac{1}{2} \sigma^S(\mathcal{R}_E) \mathbf{F}^S \dot{\mathbf{X}}^F \otimes \dot{\mathbf{X}}^F, \quad \mathcal{R}_E = \{\rho^F, \mathbf{F}^S, T\}, \quad (41)$$

$$\mathbf{P}^F = \mathbf{P}_0^F(\mathcal{R}_E, \Delta_n) + \frac{1}{2} \sigma^F(\mathcal{R}_E) \mathbf{F}^S \dot{\mathbf{X}}^F \otimes \dot{\mathbf{X}}^F, \quad n_E = n_E(\mathcal{R}_E), \quad (42)$$

– internal energy and entropy

$$\rho\varepsilon = \rho\varepsilon_0(\mathcal{R}_E, \Delta_n) + \frac{1}{2}\varepsilon_d(\mathcal{R}_E) \left(\mathbf{F}^S \dot{\mathbf{X}}^F \right) \cdot \left(\mathbf{F}^S \dot{\mathbf{X}}^F \right), \quad (43)$$

$$\rho\eta = \rho\eta_0(\mathcal{R}_E, \Delta_n) + \frac{1}{2}\eta_d(\mathcal{R}_E) \left(\mathbf{F}^S \dot{\mathbf{X}}^F \right) \cdot \left(\mathbf{F}^S \dot{\mathbf{X}}^F \right), \quad (44)$$

– fluxes of energy, entropy, porosity

$$\begin{aligned} \mathbf{Q} &= Q_V \dot{\mathbf{X}}^F - K \mathbf{G} + Q_n \mathbf{N} + Q_a \mathbf{F}^{ST} \mathbf{a}_r, \\ \mathbf{H} &= H_V \dot{\mathbf{X}}^F + H_T \mathbf{G} + H_n \mathbf{N} + H_a \mathbf{F}^{ST} \mathbf{a}_r, \\ \mathbf{J} &= \Phi \dot{\mathbf{X}}^F + J_T \mathbf{G} + J_n \mathbf{N} + J_a \mathbf{F}^{ST} \mathbf{a}_r, \end{aligned} \quad (45)$$

where all coefficients are functions of variables \mathcal{R}_E ,

– momentum source

$$\mathbf{F}^{ST} \hat{\mathbf{p}} = \Pi_V \dot{\mathbf{X}}^F + \Pi_T \mathbf{G} + \Pi_n \mathbf{N} - \rho_{12}^0 \mathbf{F}^{ST} \mathbf{a}_r, \quad \hat{\mathbf{p}} \equiv \hat{\mathbf{p}}^S, \quad (46)$$

with coefficients dependent again on variables \mathcal{R}_E .

Hence, we allow for a quadratic dependence on the diffusion velocity $\dot{\mathbf{X}}^F$ in the internal energy, entropy and partial stresses and only for the linear dependence on this velocity in vectorial quantities. This is, of course, the consequence of the isotropy assumption and yields an obvious lack of equipresence in these relations. The latter is also related to physical arguments which we proceed to present and, simultaneously, it yields considerable technical simplifications.

Nonlinear contributions of diffusion velocity $\dot{\mathbf{X}}^F$ to the internal energy and entropy (material parameters ε_d and η_d) are related to analogous terms in partial stress tensors (material parameters σ^S and σ^F). We shall find their connections after the exploitation of the entropy inequality. The physical motivation for such terms follows from the analysis of microstructure. Namely, the volume averaging shows that the macroscopic momenta $\rho^S \dot{\mathbf{x}}^S, \rho^F \dot{\mathbf{x}}^F$ do not account for rapid changes of directions of true microscopic velocities (compare remarks in the Introduction). These may be considered to be fluctuations of partial momenta caused by the tortuosity, i.e. by the curvy character of channels in porous materials. Such fluctuations are one of the reasons for dissipation of acoustic waves and create a kind of geometrical viscosity of the diffusive flow even in the case of ideal fluids in an elastic porous matrix.

Simultaneously, the internal energy and the entropy do not depend on \mathbf{G}, \mathbf{N} and \mathbf{a}_r . They are scalars and as such cannot depend in a linear way on vectors. There exists also no clear argument that they should depend in a nonlinear way on these variables.

Obviously, coefficients K and H_T are related to the usual thermal conductivity.

Coefficients Q_V and H_V are responsible for diffusive fluxes of energy and entropy. Explicit relations (19), (20) and (36) following from the definitions of bulk quantities are compatible with (45) only if we neglect nonlinear contributions in $\dot{\mathbf{X}}^F$ and leave out anisotropic effects caused by shear stresses. We do not need to go deeply into these simplifications because the bulk fluxes specified by the above constitutive relations will be not related to their partial counterparts within this model. Such a relation may be important if we consider field equations based on partial energy balance equations and this

would be the case when the components had different temperatures. However, one should stress that certain processes in granular materials are related to a nonlinear dependence of momentum source (diffusive force) on the relative velocity of components. This concerns, for instance, the liquefaction and piping of soils. A model describing such processes must be nonlinear in diffusion velocity which is natural as these velocities are large during the liquefaction.

Coefficients Q_n, Q_a in the flux \mathbf{Q} and H_n, H_a in the flux \mathbf{H} follow from the extension of the model to a constitutive dependence on heterogeneity of porosity and on relative acceleration. We discuss them after the presentation of thermodynamic identities following from the second law.

The structure of the relation for the momentum source is similar. The coefficient Π_V corresponds to the classical diffusion force. The coefficient Π_n relates the source to the heterogeneity of porosity. We shall see that, similarly to the contribution with the coupling coefficient ρ_{12}^0 , this contribution is nondissipative.

Simplification with respect to the dependence on Δ_n has not been yet fully exposed. Dependence on this field does not appear in vectorial fluxes but it is present in the energy contribution ε_0 , entropy contribution η_0 and both partial stresses $\mathbf{P}_0^S, \mathbf{P}_0^F$. We return to this dependence in the next Section.

5 Thermodynamical results

We skip here details of a rather tedious analysis of the entropy inequality and present only the most important results. These are proven in the work [30].

First of all, it can be shown that the dissipation in two-component poroelastic materials described by the set (32) of constitutive variables (without ρ^S !) is defined by the relation

$$\begin{aligned} \mathcal{D} := & \left(\frac{\partial H_V}{\partial T} - \frac{1}{T} \frac{\partial Q_V}{\partial T} + \Pi_T \right) \dot{\mathbf{X}}^F \cdot \mathbf{G} + \frac{K}{T} \mathbf{G} \cdot \mathbf{G} + \\ & + \frac{1}{T} \Pi_V \dot{\mathbf{X}}^F \cdot \dot{\mathbf{X}}^F + \Lambda_n \hat{n} \geq 0, \quad \text{for all } \mathbf{G} \text{ and } \dot{\mathbf{X}}^F. \end{aligned} \quad (47)$$

Hence, the state of thermodynamical equilibrium defined by $\mathcal{D} = 0$ appears if

$$\mathbf{G} = 0, \quad \dot{\mathbf{X}}^F = 0, \quad \hat{n} = 0. \quad (48)$$

Simultaneously, the source of porosity is described by the relation

$$\hat{n} = -\frac{\Delta_n}{\tau}, \quad \tau = \tau(\mathcal{R}_E), \quad (49)$$

and the multiplier Λ_n is also a linear function of Δ_n .

Obviously, the inequality (47) yields the following restrictions on transport coefficients

$$\Pi_V \geq 0, \quad K \geq 0, \quad \left(\frac{\partial H_V}{\partial T} - \frac{1}{T} \frac{\partial Q_V}{\partial T} + \Pi_T \right)^2 \leq 4\Pi_V \frac{K}{T^2}. \quad (50)$$

The first two inequalities are obvious. They express the classical statements that the diffusion coefficient and the heat conduction coefficient are non-negative which means that

the diffusive force points in the direction of diffusive flow and the heat flux is oriented from the hotter to colder regions. The last restriction limits the relation between Q_V and H_V , i.e. between couplings of the heat flux and the entropy flux to diffusion (thermodiffusion). In general, one cannot say more about this relation.

The important feature of the dissipation relation (47) is the lack of contribution of the relative acceleration to this quantity. This follows from the nonlinear contribution to the relative acceleration (29) which shifts the corresponding term to partial stresses (see further). It seems to rule out a rather common argument that the contribution of the relative acceleration may account for the tortuosity of the porous material. Tortuosity yields fluctuations of true momentum of the fluid component and, for this reason, scattering of acoustic waves and irreversibility of processes. It is rather obvious that the additional resistance to the diffusive flow created by the curvy character of channels must yield a dissipation which is not the case in the present model. Further nonlinearities could improve the situation but, as they must be much smaller than these for which we account for, such a formal solution does not seem to be appropriate either and one has to account for tortuosity in a model in a different way. The most probable place where one can introduce this effect is the permeability, i.e. the diffusive force.

Inequality (47) indicates that a deviation from equilibrium is described by the variables: Lagrangian velocity $\dot{\mathbf{X}}^F$ (diffusion), temperature gradient $\mathbf{G} = \text{Grad } T$ (thermal conduction), deviation of porosity Δ_n (relaxation of porosity). As already mentioned the relative acceleration \mathbf{a}_r and the gradient of porosity $\mathbf{N} = \text{Grad } n$ do not contribute to the dissipation.

Secondly, the entropy inequality yields the existence of the following potential

$$\begin{aligned} \psi &= \varepsilon - T\eta, & \rho\psi &= \rho\psi_E - \frac{1}{2}\lambda^n T \Delta_n^2 + \frac{1}{2}\rho_{12}^0 \left(\mathbf{F}^S \dot{\mathbf{X}}^S \right) \cdot \left(\mathbf{F}^S \dot{\mathbf{X}}^S \right), \\ \psi_E &= \psi_E(\mathcal{R}_E), & \lambda^n &= \lambda^n(\mathcal{R}_E), \end{aligned} \quad (51)$$

which plays a role of the Helmholtz free energy function. In contrast to classical results of thermoelasticity, it possesses nonequilibrium contributions due to the diffusion and nonequilibrium changes of porosity. In addition

$$\eta_d = 0, \quad \rho_{12}^0 = \text{const.} \quad (52)$$

Simultaneously, the coefficients of partial stresses must satisfy the following relations

$$\sigma^S = -2\mathfrak{z}\rho_{12}^0, \quad \sigma^F = -2(1 - \mathfrak{z})\rho_{12}^0. \quad (53)$$

Hence, they are influenced by both parameters of the relative acceleration. Partial stresses \mathbf{P}_0^S and \mathbf{P}_0^F become also fairly explicit.

Tedious calculations [30] yield for isotropic materials the following results for fluxes

$$\begin{aligned} \mathbf{J} &= \Phi \dot{\mathbf{X}}^F, \\ \mathbf{H} &= H_V \dot{\mathbf{X}}^F + \frac{1}{T} (-K \mathbf{G} + Q_n \mathbf{N} + Q_a \mathbf{A}), \\ \mathbf{Q} &= Q_V \dot{\mathbf{X}}^F - K \mathbf{G} + Q_n \mathbf{N} + Q_a \mathbf{A}, \quad \text{i.e.} \\ \mathbf{H} - \frac{1}{T} \mathbf{Q} &= \left(H_V - \frac{1}{T} Q_V \right) \dot{\mathbf{X}}^F. \end{aligned} \quad (54)$$

Hence, changes of porosity are caused only by diffusion (the flux \mathbf{J}) and by the sources $\hat{n} = -\Delta_n/\tau$. In the case of the simple mixture model in which there is no constitutive dependence on the gradient of porosity (see: [20]) the difference $H_V - \frac{1}{T}Q_V$ is described by the partial free energy of the fluid. In the more general case considered in this work such a relation does not follow from the second law of thermodynamics. Some additional restrictions for isotropic materials on H_V and Q_V shall not be presented here.

Constitutive relations for partial stresses can be written in the following form

$$\begin{aligned} \mathbf{P}^F = & -\rho^F \rho \frac{\partial \psi_E}{\partial \rho^F} \mathbf{F}^{S-1} + \\ & -T \left(H_V - \frac{Q_V}{T} \right) \mathbf{F}^{S-T} + T \lambda^n \Phi \Delta_n \mathbf{F}^{S-T} - \frac{\rho^F}{\rho} \rho_{12}^0 \mathbf{F}^S \dot{\mathbf{X}}^F \otimes \dot{\mathbf{X}}^F, \end{aligned} \quad (55)$$

$$\begin{aligned} \mathbf{P}^S = & \rho \frac{\partial \psi_E}{\partial \mathbf{F}^S} + \\ & +T \left(H_V - \frac{Q_V}{T} \right) \mathbf{F}^{S-T} + \rho^F \rho \frac{\partial \psi_E}{\partial \rho^F} \mathbf{F}^{S-T} - T \lambda^n \Phi \Delta_n \mathbf{F}^{S-T} + \frac{\rho^F}{\rho} \rho_{12}^0 \mathbf{F}^S \dot{\mathbf{X}}^F \otimes \dot{\mathbf{X}}^F. \end{aligned} \quad (56)$$

These Piola-Kirchhoff stresses are related to the Cauchy partial stresses by the following relations

$$\mathbf{T}^F = J^{S-1} \mathbf{P}^F \mathbf{F}^{ST}, \quad \mathbf{T}^S = J^{S-1} \mathbf{P}^S \mathbf{F}^{ST}. \quad (57)$$

Consequently, the partial Cauchy stress in the fluid \mathbf{T}^F is spherical except of the contribution of relative velocities

$$\mathbf{T}^F = -p^F \mathbf{1} - \frac{\rho^F}{\rho} \rho_{12}^0 (\dot{\mathbf{x}}^F - \dot{\mathbf{x}}^S) \otimes (\dot{\mathbf{x}}^F - \dot{\mathbf{x}}^S). \quad (58)$$

This anisotropic effect is related to the contribution of the relative acceleration to momentum source.

On the other hand, it is obvious that the free energy $\psi_E = \psi_E(\mathcal{R}_E)$ is not a potential for partial stresses but it contributes to the coupling of partial stresses. This is an important property. In contrast to the simple mixture model [20], one can now incorporate couplings characteristic for the linear Biot model which we briefly present in the next Section of this work.

6 Biot's model

The set of nonlinear field equations derived in the previous Section serves, among other applications like description of propagation of nonlinear waves or energy transport under large deformations, the purpose of control of correctness of various linear approximations. These are usually obtained by making the following assumptions

i) small deformations of components; for a two-component system this condition has the form

$$\begin{aligned} \max \{ |\lambda_\alpha^S| \}_{\alpha=1}^3 \ll 1, \quad \text{where} \quad \det(\mathbf{e}^S - \lambda_\alpha^S \mathbf{1}) = 0, \\ \left| \frac{\rho_0^F - \rho^F}{\rho_0^F} \right| \ll 1, \end{aligned} \quad (59)$$

and, obviously, λ_α^S are eigenvalues (principal stretches) of Almansi-Hamel deformation tensor, \mathbf{e}^S ,

$$\mathbf{e}^S = \frac{1}{2} (\mathbf{1} - \mathbf{B}^{S-1}), \quad \mathbf{B}^S = \mathbf{F}^S \mathbf{F}^{ST}, \quad (60)$$

while $(\rho_0^F - \rho^F) / \rho_0^F$ measures volume changes of the fluid for small deformations,
ii) deviations of temperature are small

$$\frac{|T - T_0|}{T_0} \ll 1, \quad (61)$$

iii) quadratic contributions of velocity are negligible. This concerns, in particular, convective terms.

These conditions are fulfilled, for example, by the famous Biot model of saturated porous materials (e.g. [24, 25]). In addition to the above assumptions, in Biot's model it is assumed that processes are isothermal and, consequently, the energy balance equation does not appear. For changes of porosity one assumes that the source term vanishes

$$\hat{n} = 0 \quad \implies \quad \frac{\partial \Delta_n}{\partial t} + \Phi \operatorname{div} (\mathbf{v}^F - \mathbf{v}^S) = 0, \quad (62)$$

where Φ is a constant. Then partial mass balance equations allow to integrate this porosity equation. Namely

$$\begin{aligned} \frac{\partial \rho^S}{\partial t} + \rho_0^S \operatorname{div} \mathbf{v}^S = 0 &\implies \operatorname{div} \mathbf{v}^S = -\frac{\partial}{\partial t} \left(\frac{\rho^S - \rho_0^S}{\rho_0^S} \right) = \frac{\partial e}{\partial t}, \quad e = \operatorname{tr} \mathbf{e}^S, \\ \frac{\partial \rho^F}{\partial t} + \rho_0^F \operatorname{div} \mathbf{v}^F = 0 &\implies \operatorname{div} \mathbf{v}^F = -\frac{\partial}{\partial t} \left(\frac{\rho^F - \rho_0^F}{\rho_0^F} \right) = \frac{\partial \varepsilon}{\partial t}, \quad \varepsilon = \frac{\rho_0^F - \rho^F}{\rho_0^F}, \end{aligned} \quad (63)$$

and we obtain

$$n = n_E + \Phi (\varepsilon - e) = n_0 [1 + \delta e + \gamma (\varepsilon - e)], \quad \gamma = \frac{\Phi}{n_0}, \quad (64)$$

where δ is a material parameter describing equilibrium ($e = \varepsilon$) changes of porosity due to volume changes of skeleton, measured by e , and γ is a material parameter for nonequilibrium changes of porosity, caused by diffusion (a so-called increment of fluid content). These two parameters can be derived within Biot's model by means of other material parameters of the model (see: [26]).

The above analysis shows that porosity can be ignored as a field in Biot's model.

In the original formulation, Biot is using displacements \mathbf{u} and \mathbf{U} for the skeleton and the fluid component, respectively., Then

$$\begin{aligned} \mathbf{v}^S &= \frac{\partial \mathbf{u}}{\partial t}, \quad \mathbf{e}^S = \frac{1}{2} \left(\operatorname{grad} \mathbf{u} + (\operatorname{grad} \mathbf{u})^T \right) = \operatorname{sym} \operatorname{grad} \mathbf{u}, \\ \mathbf{v}^F &= \frac{\partial \mathbf{U}}{\partial t}, \quad \varepsilon = \operatorname{div} \mathbf{U}. \end{aligned} \quad (65)$$

The displacement \mathbf{U} is a bit unusual in the description of motion of a fluid but this does not have any practical bearing.

The operators div , grad refer to differentiation in Eulerian coordinates.

The fundamental equations proposed by Biot can be then written in the following form:

$$\begin{aligned}\rho^S \frac{\partial^2 \mathbf{u}}{\partial t^2} &= \operatorname{div} \mathbf{T}^S + \pi \left(\frac{\partial \mathbf{U}}{\partial t} - \frac{\partial \mathbf{u}}{\partial t} \right) - \rho_{12} \left(\frac{\partial^2 \mathbf{U}}{\partial t^2} - \frac{\partial^2 \mathbf{u}}{\partial t^2} \right), \\ \rho^F \frac{\partial^2 \mathbf{U}}{\partial t^2} &= -\operatorname{grad} p^F - \pi \left(\frac{\partial \mathbf{U}}{\partial t} - \frac{\partial \mathbf{u}}{\partial t} \right) + \rho_{12} \left(\frac{\partial^2 \mathbf{U}}{\partial t^2} - \frac{\partial^2 \mathbf{u}}{\partial t^2} \right),\end{aligned}\quad (66)$$

where

$$\begin{aligned}\mathbf{T}^S &= \mathbf{T}_0^S + (P - 2N) (\operatorname{div} \mathbf{u}) \mathbf{1} + 2N \operatorname{sym} \operatorname{grad} \mathbf{u} + Q (\operatorname{div} \mathbf{U}) \mathbf{1}, \\ p^F &= p_0^F - Q \operatorname{div} \mathbf{u} - R \operatorname{div} \mathbf{U},\end{aligned}\quad (67)$$

The choice of material parameters P, N, R, Q describing constitutive relations for partial stresses is arbitrary. Biot himself was changing his notation from one work to the other. In the standard notation of elasticity we have $P - 2N = \lambda$, $2N = \mu$, where λ, μ are Lamé constants and R is the compressibility of the fluid. An essential extension of the set of parameters which characterize separate components (i.e. P, N for the skeleton and R for the fluid) is the parameter Q which introduces a coupling between partial stresses.

Initial partial mass densities ρ_0^S and ρ_0^F were denoted in a different way by Biot. We introduce them here in order to expose the presence of the relative acceleration which appears with the material parameter ρ_{12} . It corresponds to the coefficient ρ_{12}^0 of the nonlinear model of Sec. 4. This contribution was introduced by Biot in order to account for added mass effects which he expected to appear in diffusive processes due to a complex geometry of microstructure of porous materials. The permeability coefficient π was also introduced in a different form by Biot. It corresponds to Π_V in the nonlinear model of Sec. 4. It was argued that this coefficient describing a reaction on relative motion of components should be dependent on the true viscosity of fluid and, primarily, on the frequency of waves. The latter was attributed by Biot to the tortuosity. Finally, Biot was considering increments of stresses with respect to constant initial stresses but he never mentioned this in an explicit form. For this reason, relations (67) contain initial stresses \mathbf{T}_0^S, p_0^F .

Relations (67) do not account for an additional effect derived for the nonlinear model of the previous Section. They do not contain an influence of nonequilibrium changes of porosity Δ_n . It seems to be justified for acoustics of poroelastic materials but, on the other hand, it may be important for damage effects.

Simultaneously, the dependence on $\operatorname{Grad} n$ in the linear model can be included in constitutive relations for partial stresses. This results from the relation (64) for porosity.

Numerous theoretical and experimental papers based on Biot's model prove that Biot's intuition was right for problems of poroacoustics and that he included in his model in a correct way the most important effects appearing in poroelastic materials.

We can summarize the above presentation in the form of the following questions frequently asked in relation to Biot's model:

- (1) Is the coupling of stresses described by the material parameter Q admissible from the thermodynamic point of view?
- (2) Is the contribution of relative accelerations admissible from the point of view of material objectivity?

- (3) How are changes of porosity described by this model?
- (4) How should one write in the mathematically correct form the frequency-dependent permeability?
- (5) Can one extend in a consistent way Biot's model to large deformations of the skeleton and other nonlinear effects?

The first question is motivated by the experience with the theory of mixtures of ideal fluids. For such a mixture the coupling between partial pressures cannot be incorporated into the model in a thermodynamically admissible way if one does not account for a constitutive dependence on the so-called higher gradients. As shown in Sec. 5 the second law of thermodynamics yields for a model with constitutive dependence on $\text{Grad } n$ a result for partial stresses in which this coupling is admissible. Otherwise we get a model called the simple mixture in which there is no interaction term in constitutive relations for partial pressures (i.e. $Q \equiv 0$).

As we have already mentioned, one of the fundamental principles of any macroscopic continuum model is the so-called material frame indifference or material objectivity which states that constitutive relations should be invariant with respect to the change of observer. The relative acceleration appearing in the Biot model violates this principle and yields existence of terms in equations of motion which depend simultaneously on the choice of the reference system (i.e. observer) and on the material. However, the principle of material objectivity is fulfilled if we include non-linear contributions in the relative acceleration. In this sense, Biot's model is acceptable but it cannot describe nonlinear effects without essential changes and one cannot transform Biot's field equations to non-inertial reference frames.

Biot did not make any contributions to describe changes of porosity. There were even claims in the literature that the model does not account for such changes. We have cleared this point above.

The form of the permeability coefficient in which a dependence on a frequency of waves is incorporated cannot appear in general equations of motion which contain as well a dependence on time. Many papers on this subject avoid this problem by writing Eqs. (66) after Fourier transformation. The question arises how to incorporate such a dependence in a general case when, for instance, a complex impulse is applied as a loading and the temporal form of equations is more convenient for the formulation of the problem. The proper way to incorporate a dependence on frequency in a linear model is a hereditary integral describing diffusive forces [21].

Finally, the last question was answered in the first part of this work where it was shown that nonlinear extensions are not uniquely determined by solely adding terms to Biot's model.

7 Unsaturated porous media

We close our considerations with a remark on a problem which seems to be of primary importance in mechanics of soils and which is still open within thermodynamical modeling of porous materials.

The class of two-component models presented above applied to soils describes very important problems related to the loss of stability of slopes or damage done by earthquakes

but it is too narrow for the description of common engineering problems in which the soil is not fully saturated. In Fig. 4 we demonstrate typical situations related to flows in unsaturated soils.

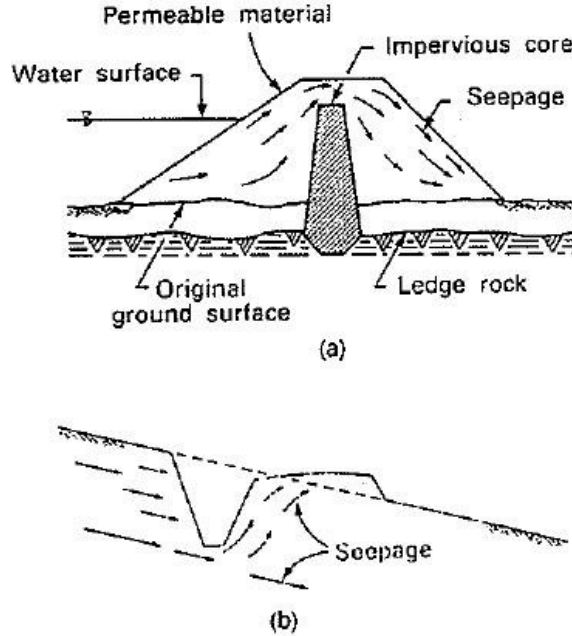


Fig. 4: *Unsaturated flow phenomena in the field*
 (a) *Earth dam with an impervious core illustrating the syphon effect;*
 (b) *interceptor ditch for a highway and a side-hill location* [27]

Formally, an extension of multicomponent models to systems with more than one fluid component is easy as we can see by inspection of equations presented already in this work. However, the problem of constitutive relations for the porous medium filled with a mixture of a liquid and a gas becomes much more complicated than it was for two-component systems. First of all, the inspection of the microstructure of such systems shows immediately that depending on the relations of volumes of the gas and the liquid we may have to deal with bubbles of gas in liquid or with droplets of liquid in the gas. The transition from one morphology to the other may appear during a flow process in which the relation of volumes of these two components changes. This is one of many difficulties related to modeling of unsaturated porous materials.

Existing three-component models are usually linear even in the case of a highly nonlinear constitutive relation describing the microstructure in such a case. Namely, in addition to porosity one has to introduce a notion of degree of saturation, S , which is a ratio of the volume of liquid in REV to the full volume of the fluid components in REV (i.e the sum of volumes of the liquid and of the gas). In the limit case $S = 1$ the porous medium is fully saturated by the liquid and in the case $S = 0$ the medium is fully saturated by the gas. This notion allows to relate partial pressures of fluid components, p^L and p^G , respectively, to true pressures, p^{LR} and p^{GR} , on the microscopic level

$$p^L = nSp^{LR}, \quad p^G = n(1 - S)p^{GR}, \quad (68)$$

with the assumption that the fluid pressure is given by the Dalton relation $p^F = p^L + p^G$. These are very strong simplifying assumptions which cannot be fulfilled, for instance, in the vicinity of the boundary. In addition, it is assumed that the degree of saturation S is given by a relation to capillary pressure, p_c , by the so-called retention curve

$$p_c = p^{GR} - p^{LR} = f(S). \quad (69)$$

The function f is assumed in different, more or less empirical forms (e.g. see [27]). In an extensive work on waves in unsaturated soils Albers [28] is using a linear approximation of the so-called van Genuchten equation

$$p_c = \frac{1}{\alpha_{vG}} [S^{(-1/m_{vG})} - 1]^{1/n_{vG}}, \quad (70)$$

where $\alpha_{vG}, m_{vG}, n_{vG}$ are material parameters.

An attempt, not very successful, to justify the relations (68) and the definition of the capillary pressure has been made by Pietruszczak and Pande (e.g. [29]).

In the work of Albers [28] the linear constitutive relations have the following form

$$\begin{aligned} \mathbf{T}^S &= \mathbf{T}_0^S + \lambda^S e \mathbf{1} + 2\mu^S \mathbf{e}^S + Q^L \varepsilon^L \mathbf{1} + Q^G \varepsilon^G \mathbf{1}, \\ p^L &= p_0^L + \rho_0^L \kappa^L \varepsilon^L + Q^L e + Q^{LG} \varepsilon^G, \\ p^G &= p_0^G + \rho_0^G \kappa^G \varepsilon^G + Q^G e + Q^{LG} \varepsilon^L, \end{aligned} \quad (71)$$

for partial stresses. In these relations, ε^L and ε^G are volume changes of the liquid and of the gas, respectively. The coefficients $\rho_0^L \kappa^L, \rho_0^G \kappa^G$ are compressibilities and the coupling coefficients are Q^L, Q^G, Q^{LG} . All these parameters are dependent on the degree of saturation and the corresponding relations are given in the work [28]. Results of the wave analysis presented in this work seem to check well with measurements. However, an appropriate thermodynamical modeling of such materials, particularly in nonlinear cases, is still an open problem.

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