

Thermomechanics of diffusive porous and granular materials

Krzysztof Wilmanski

Technische Universität Berlin and ROSE School Pavia

1 Preliminaries

The majority of materials appearing in nature and technologies is porous. These are geological materials such as rocks or soils (e.g. clays or sands), biological tissues such as bones, wood or soft tissues, many artificial materials such as ceramics, concrete, paper, granular materials such as cereals or powders, and many other. They can be divided into two large classes: nondiffusive and diffusive. Nondiffusive porous materials such as composites or some foams do not allow for the transport of mass of any substance through the solid matrix on a macroscopic level. Cavities (pores) of the matrix are closed. Diffusive porous materials such as soils, rocks, filters etc. allow for the transport of mass (fluid or gas) through the channels of the matrix. In continuum modeling procedures such porous materials are called immiscible mixtures. They are the subject of this article.

Continuous modeling of composites, or, in particular, nondiffusive porous materials is based on a classical kinematics of a one-component continuum and its main purpose is to find by an appropriate homogenization procedure a relation between their microstructure and the effective moduli that govern their macroscopic behavior. On the other hand, in modeling of diffusive porous materials the main task is to find different kinematics of solid and fluid components of such materials and material coupling between them caused by the relative motion (diffusion). The most natural way to proceed is to describe the motion of the solid matrix (skeleton) with respect to its chosen reference configuration (referential or Lagrangian description) and to describe the motion of fluid components with respect to a current configuration (spatial or Eulerian description). This yields a natural description of geometrical nonlinearities such as large deformations of the skeleton. Before we present this formalism let us point out certain flaws of models appearing in the literature under the heading of a Lagrangian description of immiscible mixtures. In continuous models it is the most essential issue to identify an infinitesimal neighborhood of a current position of particles within which these particles interact. This has been recognized by C. Truesdell in his theory of miscible mixtures which has been constructed in Eulerian description (for extensive references on this subject see, for instance, [13], [14]). Due to diffusion particles of different components, for instance particles of the skeleton and of the fluid in the channels run apart and, after a finite time lapse do not participate in the mutual interactions anymore. Hence, all constitutive relations of immiscible mixtures have to be defined on instantaneous infinitesimal neighborhoods of points in current configurations. From this point of view a consistent Lagrangian approach for all components is not possible

in contrast to such claims in some works on porous materials. However, one can choose one component, for instance the skeleton, for which this approach can be applied and then make it consistent by mappings to the current configurations. In the nonlinear continuum such consistency conditions are defined by the so-called pull-back and push-forward mappings. We present them in the next Section. This Section contains as well some remarks on thermodynamical restrictions of constitutive relations. In particular, the notion of the thermodynamical equilibrium and the dissipation are defined. Some results for nonlinear thermoporoelastic saturated materials are briefly presented. The next Section contains a particular case of the thermoporoelastic saturated materials undergoing small deformations. Some properties of two important material coefficients – thermal conductivity and diffusion (permeability) coefficient – are discussed. The fourth Section indicates some applications of the model of immiscible mixtures and exposes the need for extensions.

In the presentation of this article we use the boldface notation for vectors and tensors. Some relations are presented in Cartesian components as well in order to expose their structure. References are reduced to an absolute minimum. Further details and historical priorities can be found in those references.

2 Nonlinear thermoporoelasticity

The kinematics of the components of a porous medium is specified by functions describing the motion of the skeleton - the solid component and A fluid components. As mentioned above, nonlinear models of such systems are based on the Lagrangian description of motion of the skeleton. Let $\mathcal{B}_0 \subset \mathfrak{R}^3$ (\mathfrak{R}^3 – three-dimensional Euclidean space of configurations) denote a reference configuration of the skeleton at the instant of time, say, $t = 0$. Then the continuously differentiable mapping \mathbf{f}^S , the function of motion of the skeleton,

$$\mathbf{x} = \mathbf{f}^S(\mathbf{X}, t), \quad \mathbf{X} \in \mathcal{B}_0, \quad \text{i.e.} \quad x^k = f^{Sk}(X^K, t), \quad \mathbf{x} = x^k \mathbf{e}_k, \quad \mathbf{X} = X^K \mathbf{e}_K, \quad (1)$$

specifies the vector of the current position \mathbf{x} of the material point \mathbf{X} of the skeleton at the instant of time $t > 0$; $\mathbf{X} = \mathbf{f}^S(\mathbf{X}, 0)$. $\{\mathbf{e}_k\}$ and $\{\mathbf{e}_K\}$ are the base vectors of Eulerian and Lagrangian coordinates, respectively. For the purpose of this article it is sufficient to assume that these are Cartesian coordinates. The above definition is identical with the definition of the function of motion of a usual continuous medium (e.g. [11]). By means of this function we can define the deformation gradient \mathbf{F}^S and the velocity $\dot{\mathbf{x}}^S$ of the skeleton

$$\mathbf{F}^S = \text{Grad } \mathbf{f}^S, \quad \dot{\mathbf{x}}^S = \frac{\partial \mathbf{f}^S}{\partial t}, \quad \text{i.e.} \quad F_K^{Sk} = \frac{\partial f^{Sk}}{\partial X^K}, \quad \dot{x}^{Sk} = \frac{\partial f^{Sk}}{\partial t}. \quad (2)$$

As usual, the deformation gradient specifies the (linear) transformation rule for material vectors. Its squares define the right and left Cauchy-Green deformation measures

$$\mathbf{C}^S = \mathbf{F}^{ST} \mathbf{F}^S, \quad \mathbf{c}^S = \mathbf{F}^S \mathbf{F}^{ST}, \quad \text{i.e.} \quad C_{KL}^S = F_K^{Sk} F_{kL}^S, \quad c_{kl}^S = F_k^{SK} F_{lK}^S. \quad (3)$$

We shall not go into any further details of the kinematics because they do not differ from the classical description of a single-component continuum.

As already mentioned, the kinematics of the fluid components filling the channels of the skeleton is described in a natural way by the Eulerian approach typical for fluids.

This means that at each point occupied in the current configuration by a material point of the α -component, $\alpha \in (1, \dots, A)$, the velocity field \mathbf{v}^α should be given

$$\mathbf{v}^\alpha = \mathbf{v}^\alpha(\mathbf{x}, t), \quad \mathbf{x} \in \mathcal{B}_t = \{\mathbf{x} \in \mathbb{R}^3 \mid \mathbf{x} = \mathbf{f}^S(\mathbf{X}, t), \mathbf{X} \in \mathcal{B}_0\}. \quad (4)$$

These vector functions are defined on a set \mathcal{B}_t which is the current configuration of the skeleton at the instant of time t . This means that at each point of this set material points of all components of the porous medium appear simultaneously. This property of the continuum theory of mixtures was introduced by C. Truesdell in 1957. Obviously, it is a necessary condition for the construction of a field theory describing such media. Otherwise, unknown fields would not be defined on the same space of independent variables, such notions as continuity or differentiability could not be introduced and the mathematical model would not be consistent. This point of the theory of porous media, called also the theory of immiscible mixtures, is very often misinterpreted in the literature, particularly in publications on soil mechanics in which boundary value problems are not considered and the flaws of the model with different sets of material points for each component are not clearly visible.

In order to obtain a consistent mathematical model we have to transform independent variables in the relation (4). Namely, we define the velocity fields for fluid components by the following relation

$$\hat{\mathbf{x}}^\alpha = \mathbf{v}^\alpha(\mathbf{f}^S(\mathbf{X}, t), t) = \hat{\mathbf{x}}^\alpha(\mathbf{X}, t), \quad \alpha \in (1, \dots, A), \quad \text{i.e.} \quad \dot{x}^{\alpha k} = \dot{x}^{\alpha k}(X^K, t). \quad (5)$$

This is a part of the so-called pull-back operation which specifies velocity fields on the reference configuration of the skeleton. Detailed descriptions of this operation and of the inverse push-forward operation can be found in the book of J. Marsden and T. Hughes [8].

Now we are in the position to define the set of unknown fields describing an immiscible mixture with A fluid components. It is clear that the function of motion of the skeleton and the velocity fields of the fluid components must enter this set. In addition, as in the case of the Eulerian description of fluids, mass densities are basic unknowns. We denote them by $\rho^S, \rho^\alpha, \alpha \in (1, \dots, A)$, where the first one is the partial mass density of the skeleton and the remaining are partial mass densities of the fluid components. They specify the mass of the corresponding component per unit volume of the reference configuration \mathcal{B}_0 at the instant of time t . The mass density of the skeleton would not enter this set, as it is the case in the classical Lagrangian description of single-component continua, if a mass exchange between components were absent. We return to this point in the sequel.

The above fields would be sufficient for the construction of a model of isothermal processes in miscible mixtures (mixtures of fluids). For immiscible mixtures it is not the case. The reason is the microstructure which makes mixtures immiscible. Complex geometries of the channels in the solid matrix, solid fibers, voids of different shapes and size, influence the mechanical properties of the skeleton (e.g. they yield anisotropy of bones). Simultaneously, they yield complex flows of fluids in curvy channels, interactions of fluid components with surfaces of channels (e.g. wetting properties) etc. A general continuous model accounting for all these properties would be of a hopeless complexity. For this reason, various special models are constructed in which only some of the microstructural properties are incorporated. The most popular is an isotropic model of a porous material fully saturated with a single fluid component. Then the additional microstructural

variable is the porosity n , i.e. the fraction of the volume of the voids in the volume of the microstructural domain called the Representative Elementary Volume (*REV*). The latter is considered to be large enough to allow the calculation of volume averages of random microstructural properties and small enough to be considered to be a material point of the continuum macroscopic model (compare [2]). We present further some other microstructural variables.

For nonisothermal processes a notion of a temperature or many temperatures must be introduced. This is still very much an open problem of thermodynamics of immiscible mixtures. The assumption that the porous medium is described by a single temperature means that the system is in local thermodynamical equilibrium. Many systems do not fulfil this assumption. For the purpose of this Section we introduce the notion of partial temperatures of the components. There are numerous unsolved problems related to such a model – the physical interpretation of partial temperatures (they cannot be identified by measurements on the so-called ideal walls), the formulation of boundary conditions for multiple heat conduction equations, etc.

Bearing the above remarks in mind we can set the problem of continuous modeling of thermoporoelastic materials as the formulation of field equations for the following quantities

$$\mathcal{F} = \{ \mathbf{f}^S, \dot{\mathbf{x}}^1, \dots, \dot{\mathbf{x}}^A, \rho^S, \rho^1, \dots, \rho^A, n, \theta^S, \theta^1, \dots, \theta^A \}, \quad (6)$$

which are functions of the points $\mathbf{X} \in \mathcal{B}_0$ and time t . $\theta^S, \theta^1, \dots, \theta^A$ are temperatures of the components. For those $5(1 + A) + 1$ fields field equations follow from local balance equations. However, in many cases of practical importance additional fields and additional field equations must be formulated. This is the case when there appears a mass exchange between the components due to chemical reactions or phase transformations. Then some evolution equations for the extent of such reactions must be formulated. This is also the case when irreversible deformations such as plastic or viscoplastic deformations appear. In those cases flow rules must be added. In this short article we shall not present such relations.

Balance equations and partial conservation laws are formulated on material domains of the components. Then time changes of such quantities as mass, momentum, energy, etc. are given by surface fluxes, volume supplies and sources. Consequently, we have to define first the material domains for all components of immiscible mixtures. In general, for components S or $\alpha \in (1, \dots, A)$ these are subsets of the current configurations \mathcal{B}_t in the space of configuration \mathcal{R}^3 whose boundaries move with the velocity $\dot{\mathbf{x}}^S$ or $\dot{\mathbf{x}}^\alpha$, respectively. Projected by the function of motion \mathbf{f}^{S-1} on the reference configuration \mathcal{B}_0 these yield either subsets of \mathcal{B}_0 which do not change in time – for the skeleton, or subsets of \mathcal{B}_0 whose boundaries move with the so-called Lagrangian diffusion velocities $\dot{\mathbf{X}}^\alpha$ for the fluid components. These velocities are defined by the relation

$$\dot{\mathbf{X}}^\alpha = \mathbf{F}^{S-1} (\dot{\mathbf{x}}^\alpha - \dot{\mathbf{x}}^S), \quad (7)$$

(compare [13], [14] for details). Then the balance laws have the following local form

1. mass balances

$$\frac{\partial \rho^S}{\partial t} - \hat{\rho}^S = 0, \quad \frac{\partial \rho^\alpha}{\partial t} + \text{Div } \rho^\alpha \dot{\mathbf{X}}^\alpha - \hat{\rho}^\alpha = 0, \quad \hat{\rho}^S + \sum_{\alpha=1}^A \hat{\rho}^\alpha = 0, \quad (8)$$

2. momentum balances

$$\begin{aligned} \frac{\partial \rho^S \dot{\mathbf{x}}^S}{\partial t} - \text{Div } \mathbf{P}^S - \hat{\mathbf{p}}^S - \rho^S \mathbf{b}^S &= 0, \\ \frac{\partial \rho^\alpha \dot{\mathbf{x}}^\alpha}{\partial t} + \text{Div } \rho^\alpha \dot{\mathbf{x}}^\alpha \otimes \dot{\mathbf{X}}^\alpha - \text{Div } \mathbf{P}^\alpha - \hat{\mathbf{p}}^\alpha - \rho^\alpha \mathbf{b}^\alpha &= 0, \\ \hat{\mathbf{p}}^S + \sum_{\alpha=1}^A \hat{\mathbf{p}}^\alpha &= 0, \end{aligned} \quad (9)$$

3. energy balances

$$\begin{aligned} \frac{\partial}{\partial t} \left(\rho^S \varepsilon^S + \frac{1}{2} \rho^S \dot{\mathbf{x}}^S \cdot \dot{\mathbf{x}}^S \right) + \text{Div} (\mathbf{Q}^S - \mathbf{P}^{ST} \dot{\mathbf{x}}^S) - \\ - \rho^S (\mathbf{b}^S \cdot \dot{\mathbf{x}}^S + r^S) - \hat{\varepsilon}^S &= 0, \\ \frac{\partial}{\partial t} \left(\rho^\alpha \varepsilon^\alpha + \frac{1}{2} \rho^\alpha \dot{\mathbf{x}}^\alpha \cdot \dot{\mathbf{x}}^\alpha \right) + \text{Div} \left[\left(\rho^\alpha \varepsilon^\alpha + \frac{1}{2} \rho^\alpha \dot{\mathbf{x}}^\alpha \cdot \dot{\mathbf{x}}^\alpha \right) \dot{\mathbf{X}}^\alpha + \right. \\ \left. + \mathbf{Q}^\alpha - \mathbf{P}^{\alpha T} \dot{\mathbf{x}}^\alpha \right] - \rho^\alpha (\mathbf{b}^\alpha \cdot \dot{\mathbf{x}}^\alpha + r^\alpha) - \hat{\varepsilon}^\alpha &= 0, \quad \hat{\varepsilon}^S + \sum_{\alpha=1}^A \hat{\varepsilon}^\alpha = 0, \end{aligned} \quad (10)$$

4. porosity balance

$$\frac{\partial (n - n_E)}{\partial t} + \text{Div } \mathbf{J} - \hat{n} = 0. \quad (11)$$

We use the following notation: quantities with hats are the intensities of sources per unit reference volume and time, $\mathbf{P}^S, \mathbf{P}^\alpha$ are partial Piola-Kirchhoff stress tensors, $\mathbf{b}^S, \mathbf{b}^\alpha$ are body forces which include noninertial contributions for arbitrary reference systems in the configuration space, $\varepsilon^S, \varepsilon^\alpha$ are specific partial internal energies of the components, $\mathbf{Q}^S, \mathbf{Q}^\alpha$ are partial heat flux vectors per unit reference surface, r^S, r^α are partial radiation intensities, n_E is the equilibrium porosity and \mathbf{J} is the porosity flux per unit reference surface.

In addition, the quantity which serves the purpose of formulation of the second law of thermodynamics – the entropy density – is assumed to be given in terms of the partial entropy densities η^α which satisfy the balance law

$$\frac{\partial \rho^S \eta^S}{\partial t} + \text{Div } \mathbf{H}^S + \rho^S s^S + \hat{\eta}^S = 0, \quad \frac{\partial \rho^\alpha \eta^\alpha}{\partial t} + \text{Div } \mathbf{H}^\alpha + \rho^\alpha s^\alpha + \hat{\eta}^\alpha = 0, \quad (12)$$

where $\mathbf{H}^S, \mathbf{H}^\alpha$ denote the partial fluxes of entropy, s^S, s^α are the partial entropy radiations. The partial source terms $\hat{\eta}^S, \hat{\eta}^\alpha$ are different from zero in thermodynamically irreversible processes.

The theory of miscible mixtures is based on a principle of compatibility which requires that the partial balance equations yield conservation laws of a single continuum with appropriate definitions of bulk quantities. The same principle is imposed on the theory of immiscible mixtures. It is satisfied provided the source terms fulfil the above conditions of conservation of mass, momentum and energy. In addition, bulk mass density, momentum density, energy density, the bulk stress tensor, the bulk heat flux vector and bulk volume

supplies are defined as sums of partial quantities with corrections nonlinear in the diffusion velocities. For instance,

$$\begin{aligned}
\rho &= \rho^S + \sum_{\alpha=1}^A \rho^\alpha, & \rho \dot{\mathbf{x}} &= \rho^S \dot{\mathbf{x}}^S + \sum_{\alpha=1}^A \rho^\alpha \dot{\mathbf{x}}^\alpha, & \rho \dot{\mathbf{X}} &:= \sum_{\alpha=1}^A \rho^\alpha \dot{\mathbf{X}}^\alpha, \\
\rho \varepsilon &= \rho^S \varepsilon^S + \sum_{\alpha=1}^A \rho^\alpha \varepsilon^\alpha + \frac{1}{2} \left\{ \rho^S \mathbf{C}^S \cdot (\dot{\mathbf{x}} \otimes \dot{\mathbf{x}}) + \sum_{\alpha=1}^A \rho^\alpha \mathbf{C}^S \cdot (\dot{\mathbf{x}}^\alpha - \dot{\mathbf{x}}) \otimes (\dot{\mathbf{x}}^\alpha - \dot{\mathbf{x}}) \right\}, \\
\mathbf{P} &= \mathbf{P}^S + \sum_{\alpha=1}^A \mathbf{P}^\alpha - \underbrace{F^S \left\{ \rho^S \dot{\mathbf{x}} \otimes \dot{\mathbf{x}} + \sum_{\alpha=1}^A \rho^\alpha (\dot{\mathbf{x}}^\alpha - \dot{\mathbf{x}}) \otimes (\dot{\mathbf{x}}^\alpha - \dot{\mathbf{x}}) \right\}}_{(13)}, \\
\mathbf{Q} &= \mathbf{Q}^S + \sum_{\alpha=1}^A \mathbf{Q}^\alpha - \\
&\quad - \underbrace{\rho^S \varepsilon^S \dot{\mathbf{x}} + \sum_{\alpha=1}^A \rho^\alpha \varepsilon^\alpha (\dot{\mathbf{x}}^\alpha - \dot{\mathbf{x}}) + \mathbf{P}^{ST} \mathbf{F}^S \dot{\mathbf{x}} - \sum_{\alpha=1}^A \mathbf{P}^{\alpha T} \mathbf{F}^S (\dot{\mathbf{x}}^\alpha - \dot{\mathbf{x}})}_{(13)} + \\
&\quad + \frac{1}{2} \left\{ -\rho^S \dot{\mathbf{x}} \otimes \dot{\mathbf{x}} \otimes \dot{\mathbf{x}} + \sum_{\alpha=1}^A \rho^\alpha (\dot{\mathbf{x}}^\alpha - \dot{\mathbf{x}}) \otimes (\dot{\mathbf{x}}^\alpha - \dot{\mathbf{x}}) \otimes (\dot{\mathbf{x}}^\alpha - \dot{\mathbf{x}}) \mathbf{C}^S \right\}.
\end{aligned}$$

The underlined parts vanish in approximate theories in which diffusion velocities are small. For example, in soils diffusion velocities are of the order of magnitude of 0.1 m/s (usually much less than that). Then the contribution of the diffusion velocities to the stress tensor are of the order of 20 – 30 Pa compared to, say, 100 kPa of the pressure of the water in the pores. The bulk Piola-Kirchhoff stress tensor \mathbf{P} and the bulk heat flux vector \mathbf{Q} play an important role in the formulation of boundary conditions for such a nonlinear theory. We do not present these problems in this short exposition.

There are $5(1 + A) + 1$ balance laws (9-11) and they can be transformed into field equations for the fields (6) by an appropriate choice of constitutive relations for the following quantities

$$\mathcal{C} = \{ \varepsilon^A, \varepsilon^\alpha, n_E, \mathbf{P}^S, \mathbf{P}^\alpha, \mathbf{Q}^A, \mathbf{Q}^\alpha, \mathbf{J}, \hat{\rho}^\alpha, \hat{\mathbf{p}}^\alpha, \hat{\varepsilon}^\alpha, \hat{n} \}, \quad \alpha = 1, \dots, A. \quad (14)$$

This choice is dependent on the purpose of the model. For instance, for thermoporoelastic materials without mass exchange between the components the set of appropriate variables is as follows

$$\mathcal{V} = \{ \rho^\alpha, \mathbf{F}^S, n, \text{Grad } n, \theta^S, \theta^\alpha, \text{Grad } \theta^S, \text{Grad } \theta^\alpha, \dot{\mathbf{X}}^\alpha \}, \quad (15)$$

and then it is assumed that the constitutive relations

$$\mathcal{C} = \mathcal{C}(\mathcal{V}), \quad (16)$$

are continuously differentiable functions. As usual, they specify the class of materials described by the model. It is an important feature of these relations that they contain a dependence on the porosity gradient $\text{Grad } n$ in addition to a dependence on the porosity n itself. Such a property is characteristic for the so-called second gradient models. In the present case, it yields the existence of couplings between components which is well

understood and physically justified within a linear model introduced by M. A. Biot and which we briefly present further in this article.

Constitutive relations should satisfy a number of restrictions which we do not discuss here in details. Among the most important conditions which should be fulfilled are

1. *the principle of material objectivity*, i.e. a requirement that constitutive relations should be invariant with respect to the change of the observer in the space of configurations: $\mathbf{x}^* = \mathbf{O}(t)\mathbf{x} + \mathbf{a}(t)$, $\mathbf{x}, \mathbf{x}^* \in \mathfrak{R}^3$, where $\mathbf{O}(t)$ is an arbitrary time dependent orthogonal matrix and $\mathbf{a}(t)$ an arbitrary time dependent vector. These are obviously the rigid time dependent rotation and the displacement of the body as a whole. They yield explicit contributions of noninertial forces to equations of motion but they should not influence constitutive material properties,

2. *the principle of material symmetry*, i.e. a requirement that constitutive relations should be invariant with respect to the transformation of reference configurations $\mathbf{X}^* = \mathbf{G}\mathbf{X}$, $\mathbf{X} \in \mathcal{B}_0$, $\mathbf{X}^* \in \{\mathbf{G}\mathbf{X} | \mathbf{X} \in \mathcal{B}_0\}$, where \mathbf{G} is an element of a unimodular group defining the symmetry of the material. This requirement is usually imposed only on the properties of the skeleton while fluids filling the pores are assumed to be isotropic,

3. *the principle of thermodynamical admissibility* which consists of the entropy inequality: $\hat{\eta} = \eta^S + \sum_{\alpha=1}^A \hat{\eta}^\alpha \geq 0$, and some conditions imposed on local equilibrium states appearing on singular surfaces modelling boundaries of media.

Technicalities yielding particular models satisfying these conditions are very complex and we shall not present them here. It should only be mentioned that the third condition which is the second law of thermodynamics yields the specification of the so-called dissipation function. It is semi-positive definite which reflects the second law of thermodynamics and it vanishes in the state of thermodynamical equilibrium. This function is at least quadratic with respect to the following variables

1. difference of the so-called partial chemical potentials which restricts the form of the mass sources,
2. diffusion velocities $\dot{\mathbf{X}}^\alpha$ which restricts the form of momentum sources; it yields a positive definiteness of the permeability tensors,
3. difference of partial temperatures $\theta^\alpha - \theta^\beta$ which restricts the form of energy sources and yields the evolution to local thermodynamical equilibria,
4. nonequilibrium changes of the porosity $n - n_E$ which restricts the evolution of microcracks and damage.

A number of identities which follow from the third principle yield as well the so-called Gibbs equation which, in turn, indicates the existence of various thermodynamical potentials such as Helmholtz free energies, Gibbs free energies, chemical potentials, etc. They simplify considerably the formulation of the constitutive relations.

Interfaces, boundaries. Partial differential equations which follow from the above construction of the model for the chosen fields (6) require the formulation of initial and boundary conditions. In many cases of practical importance such as the propagation of waves in thermoporoelastic materials the model is hyperbolic which means that the Cauchy problem is well posed. It means that one can find local solutions solely by a formulation of initial conditions. This is indeed a nice mathematical property but it has almost no practical importance for engineering problems. In real media we have to formulate conditions on boundaries of the medium. This is a quite complex problem for immiscible mixtures and its solution is only known for some particular cases. Difficulties appear already by the formulation of the notion of the boundary. In the case of porous materials it is usually assumed that boundaries are identical with the boundary of the domain \mathcal{B}_0 which is material with respect to the skeleton. It means that it does not move in the reference configuration and its motion in the current configurations is given by the velocity field of the skeleton $\dot{\mathbf{x}}^S$. However even for problems of porous materials there may arise difficulties with the definition of interfaces which, for instance, determine boundaries between saturated and unsaturated parts of the medium or fronts of freezing in soils. In addition, conditions on such surfaces are indicated by the so-called dynamic compatibility conditions only in cases of boundaries on which one can neglect the influence of boundary layers. This may be the case for impermeable boundaries (i.e. boundaries on which the relative velocities of all components are zero) but even then there may appear important contributions which are not predicted by ideal dynamic compatibility conditions. A typical example is the boundary condition for the transfer of energy through an impermeable boundary in the case of radiation and convection along the boundary. This is the typical problem for walls in civil engineering structures.

In order to appreciate the problem we demonstrate here some particular boundary conditions for porous media. As already mentioned the basis for their construction follows from dynamic compatibility conditions which result from general balance laws for singular surfaces. Let us project a surface, moving through a porous medium on which singularities appear, onto the reference configuration \mathcal{B}_0 by means of the function of motion of the skeleton \mathbf{f}^S . This surface may not be material with respect to the skeleton (e.g. a wave front) and, consequently it possesses a speed U with respect to particles of the skeleton $\mathbf{X} \in \mathcal{B}_0$ and its unit normal is \mathbf{N} . On such a surface the following conditions result from global balance equations (e.g. see [13], [14])

$$\begin{aligned}
U [[\rho^S]] &= 0, \quad \left[\left[\rho^\alpha \left(\dot{\mathbf{X}}^\alpha \cdot \mathbf{N} - \mathbf{U} \right) \right] \right] = 0, \quad \alpha \in (1, \dots, A), \\
\rho^S U [[\dot{\mathbf{x}}^S]] + [[\mathbf{P}^S]] \mathbf{N} &= \mathbf{0}, \quad \rho^\alpha \left(\dot{\mathbf{X}}^\alpha \cdot \mathbf{N} - \mathbf{U} \right) [[\dot{\mathbf{x}}^\alpha]] - [[\mathbf{P}^\alpha]] \mathbf{N} = 0, \\
\rho^S U \left[\left[\varepsilon^S + \frac{1}{2} \dot{x}^{S2} \right] \right] + [[\mathbf{P}^{ST} \dot{\mathbf{x}}^S - \mathbf{Q}^S]] \mathbf{N} &= \mathbf{0}, \\
\rho^\alpha \left(\dot{\mathbf{X}}^\alpha \cdot \mathbf{N} - \mathbf{U} \right) \left[\left[\varepsilon^\alpha + \frac{1}{2} \dot{x}^{\alpha 2} \right] \right] - [[\mathbf{P}^{\alpha T} \dot{\mathbf{x}}^\alpha - \mathbf{Q}^\alpha]] \mathbf{N} &= 0, \\
U [[n - n_E]] - [[\mathbf{J}]] \cdot \mathbf{N} &= 0,
\end{aligned} \tag{17}$$

where $[[\dots]]$ is the jump of the quantity on the surface. These relations are, respectively, partial mass, momentum, energy and porosity balances for an ideal singular surface. The surface is ideal because there are no contributions of surface terms which would appear if

surface layers were replaced by surface densities. We return to this point later.

In addition to the relations (17) the integrability condition of the deformation gradient yields the following kinematic condition

$$U [[\mathbf{F}^S]] + [[\dot{\mathbf{x}}^S]] \otimes \mathbf{N} = 0. \quad (18)$$

Ideal conditions on a surface which is material with respect to the skeleton follow with $U \equiv 0$ (hence $[[\dot{\mathbf{x}}^S]] = 0$), i.e.

$$\begin{aligned} [[\rho^\alpha \dot{\mathbf{X}}^\alpha]] \cdot \mathbf{N} &= 0, \quad [[\mathbf{P}^S]] \mathbf{N} = \mathbf{0}, \quad \rho^\alpha \dot{\mathbf{X}}^\alpha \cdot \mathbf{N} [[\dot{\mathbf{x}}^\alpha]] - [[\mathbf{P}^\alpha]] \mathbf{N} = 0, \\ [[\mathbf{Q}^S]] \mathbf{N} &= \mathbf{0}, \quad \rho^\alpha \dot{\mathbf{X}}^\alpha \cdot \mathbf{N} \left[\left[\varepsilon^\alpha + \frac{1}{2} \dot{x}^{\alpha 2} \right] \right] - [[\mathbf{P}^{\alpha T} \dot{\mathbf{x}}^\alpha - \mathbf{Q}^\alpha]] \cdot \mathbf{N} = 0, \\ [[\mathbf{J}]] \cdot \mathbf{N} &= 0. \end{aligned} \quad (19)$$

Hence, even though continuity of the partial stress vector in the skeleton, $\mathbf{P}^S \mathbf{N}$, and of the partial heat flux in the skeleton normal to the surface, $\mathbf{Q}^S \cdot \mathbf{N}$, i.e. classical continuity conditions follow in this case, the conditions for the remaining partial quantities are far from being simple. For impermeable boundaries we have $\dot{\mathbf{x}}^\alpha = \dot{\mathbf{x}}^S$, i.e. $\dot{\mathbf{X}}^\alpha = 0$, $\alpha \in (1, \dots, A)$, and, consequently, partial stress vectors in the fluid components $\mathbf{P}^\alpha \mathbf{N}$ as well as the normal components of heat flux vectors $\mathbf{Q}^\alpha \cdot \mathbf{N}$ are also continuous. This is not any more the case on permeable boundaries.

The typical example is the permeable boundary between a saturated porous medium and a viscous fluid in the exterior. The flow of this fluid along the boundary creates a boundary layer within the porous material. The contact condition for shear stresses on such a surface must account for the velocity distributions within surface layers on both sides of the boundary. This yields the so-called Beavers-Joseph boundary condition (1967). Another example is the flow in the direction perpendicular to such a surface. The relative velocity which characterizes this flow is proportional to the pressure difference between the channels in the porous material and the exterior. There appears an additional material parameter α for such a condition which characterizes the surface properties, i.e. again properties of boundary layers. For example, for a two-component linear porous material this condition has the form

$$\rho_0^F (\mathbf{v}^F - \mathbf{v}^S) \cdot \mathbf{n} \equiv \dot{m}^F = \alpha (n_0 p_{ext}^F - p^F), \quad (20)$$

where \dot{m}^F is the flux of the fluid through the boundary per unit surface and unit time, p_{ext}^F is the fluid pressure in the exterior. The constant α reflects the properties of boundary layers on both sides of the boundary. For $\alpha = 0$ the boundary is impermeable and for $\alpha \rightarrow \infty$ we obtain the condition of the continuity of pressure which follows from the ideal dynamic compatibility conditions (no boundary layers!). This type of the boundary condition is commonly used in investigations of flows through a rigid porous matrix. Such boundary conditions play a particularly important role in the analysis of surface waves in porous media – particularly, Rayleigh waves and Stoneley waves between saturated porous media and a fluid (e.g. [6]). For those waves they were introduced by H. Deresiewicz (1961).

Let us mention another example which contributes to the condition for the heat flux. Even in the case of a contact problem between a fluid and a solid processes of convection

along the boundary modify the classical Fourier continuity condition for the heat flux. A material parameter – the Nusselt number – enters the condition for the heat transfer coefficient. This is, of course, also the case for porous materials. We return later to this example.

We skip further details of nonlinear thermoporoelastic models. In this article we describe further only a linear version of such a model.

3 Linear thermoporoelastic models

In many problems of practical bearing such as thermomechanics of rocks, thermodiffusion and condensation in structural walls, propagation of acoustic waves in porous materials, the deformations of the skeleton and the fluid as well as the temperature differences are small. Then it is sufficient to construct linear models of thermoporoelastic media. Hence we can make the assumption

$$\sup \left(\|\mathbf{e}^S\|, \left| \frac{\rho^\alpha - \rho_0^\alpha}{\rho_0^\alpha} \right|, \left| \frac{\theta^\alpha - \theta_0^\alpha}{\theta_0^\alpha} \right|, |n - n_0| \right) \ll 1, \quad \mathbf{e}^S := \frac{1}{2} (\mathbf{1} - \mathbf{c}^{S-1}), \quad (21)$$

where the subscript zero denotes an initial value of the corresponding quantity. Obviously, $\mathbf{e}^S = e_{ij}^S \mathbf{e}_i \otimes \mathbf{e}_j$ is the Almansi-Hamel tensor of small deformations of the skeleton. Its norm $\|\mathbf{e}^S\|$ is defined as the maximum of the absolute value of stretches (principal values of \mathbf{e}^S). The difference of partial mass densities describes volume changes of corresponding fluid components. Under this assumption there is no distinction between Lagrangian and Eulerian description. Linearized balance equations in which nonlinear contributions of the velocities (i.e. kinematic terms and products of sources with relative velocities) must be neglected as well, have the form

$$\begin{aligned} \frac{\partial \rho^S}{\partial t} + \rho_0^S \operatorname{div} \mathbf{v}^S &= \hat{\rho}^S, & \frac{\partial \rho^\alpha}{\partial t} + \rho_0^\alpha \operatorname{div} \mathbf{v}^\alpha &= \hat{\rho}^\alpha, & \hat{\rho}^S + \sum_{\alpha=1}^A \hat{\rho}^\alpha &= 0, \\ \rho_0^S \frac{\partial \mathbf{v}^S}{\partial t} - \operatorname{div} \mathbf{T}^S &= \rho^S \mathbf{b}^S + \hat{\mathbf{p}}^S, & \rho_0^\alpha \frac{\partial \mathbf{v}^\alpha}{\partial t} - \operatorname{div} \mathbf{T}^\alpha &= \rho^\alpha \mathbf{b}^\alpha + \hat{\mathbf{p}}^\alpha, & \hat{\mathbf{p}}^S + \sum_{\alpha=1}^A \hat{\mathbf{p}}^\alpha &= 0, \\ \rho_0^S \frac{\partial \varepsilon^S}{\partial t} + \operatorname{div} \mathbf{q}^S &= \operatorname{tr} (\mathbf{T}_0^S \operatorname{grad} \mathbf{v}^S) + \rho_0^S r^S + \hat{\varepsilon}^S, & & & (22) \\ \rho_0^\alpha \frac{\partial \varepsilon^\alpha}{\partial t} + \operatorname{div} \mathbf{q}^\alpha &= \operatorname{tr} (\mathbf{T}_0^\alpha \operatorname{grad} \mathbf{v}^\alpha) + \rho_0^\alpha r^\alpha + \hat{\varepsilon}^\alpha, & \hat{\varepsilon}^S + \sum_{\alpha=1}^A \hat{\varepsilon}^\alpha &= 0, \end{aligned}$$

where the mass densities ρ^S, ρ^α , momentum densities $\rho_0^S \mathbf{v}^S, \rho_0^\alpha \mathbf{v}^\alpha$, internal energy densities $\rho_0^S \varepsilon^S, \rho_0^\alpha \varepsilon^\alpha$ refer to the unit current volume of the mixture, $\mathbf{T}^S, \mathbf{T}^\alpha$ are partial Cauchy stress tensors, $\mathbf{q}^S, \mathbf{q}^\alpha$ are partial heat flux vectors referring to a unit current surface. The differentiation is performed with respect to Eulerian coordinates x_k , i.e. $\operatorname{grad} = \mathbf{e}_k \frac{\partial}{\partial x_k}$.

Under a frequently made assumption of the common temperature of all components (local thermodynamical equilibrium of the mixture) energy sources vanish and the bulk energy conservation law replaces the partial energy balance laws. It has the following

form

$$\begin{aligned} \rho_0 \frac{\partial \varepsilon}{\partial t} + \operatorname{div} \mathbf{q} &= \operatorname{tr} (\mathbf{T}_0 \operatorname{grad} \mathbf{v}) + \rho_0 r, \\ \rho_0 &= \rho_0^S + \sum_{\alpha=1}^A \rho_0^\alpha, \quad \rho_0 \varepsilon = \rho_0^S \varepsilon^S + \sum_{\alpha=1}^A \rho_0^\alpha \varepsilon^\alpha, \quad \rho_0 r = \rho_0^S r^S + \sum_{\alpha=1}^A \rho_0^\alpha r^\alpha, \\ \mathbf{q} &= \mathbf{q}^S + \sum_{\alpha=1}^A \mathbf{q}^\alpha, \quad \mathbf{T}_0 = \mathbf{T}_0^S + \sum_{\alpha=1}^A \mathbf{T}_0^\alpha. \end{aligned} \quad (23)$$

The porosity balance equation (11) reduces in the linear model to the form

$$\frac{\partial (n - n_E)}{\partial t} + \sum_{\alpha=1}^A \Phi^\alpha \operatorname{grad} (\mathbf{v}^\alpha - \mathbf{v}^S) - \hat{n} = 0. \quad (24)$$

The matrices $\Phi^\alpha, \alpha \in (1, \dots, A)$ are constant. In the isotropic case they reduce to A constants.

The above set of equations supplemented by linear constitutive relations yields a model of reactive transport in porous media [7]. We do not present here any details of such a model. It requires a discussion of the problem of mass sources which are described by evolution laws. These may result from chemical reactions, phase changes (e.g. evaporation and condensation) or adsorption (e.g. Langmuir adsorption of impurities on walls of channels). However it should be stressed that, in spite of a nonisothermal character of such processes the question of thermal stresses, particularly in rocks, has been as yet fully ignored.

Another simplification of the general model which has been very extensively investigated in the literature is an isothermal model of partially saturated porous media without mass sources. The fluid in channels consists in this case of two (or more) immiscible components whose contribution to such a mixture is specified by the degree of saturation which is related to the capillary pressure on interfaces between the fluid components. For this model a coupling between the relative motion of the components and acoustic waves was considered. Again thermal stresses were ignored. The simplest version of this model, in which the degree of saturation is either one or zero, was proposed by M. A. Biot (see the collection of Biot's papers on porous materials published by I. Tolstoy [10]). The constitutive equations of this model have the following form

$$\begin{aligned} \mathbf{T}^S &= \mathbf{T}_0^S + \lambda^S e \mathbf{1} + 2\mu^S \mathbf{e}^S + Q \varepsilon \mathbf{1}, \quad p^F = p_0^F - Q e - \rho_0^F \kappa \varepsilon, \\ \hat{\mathbf{p}}^S &= -\hat{\mathbf{p}}^F = \pi (\mathbf{v}^F - \mathbf{v}^S), \quad \hat{n} = 0, \\ n_E &= n_0 (1 + \delta e), \quad e = \operatorname{tr} \mathbf{e}^S = \frac{\rho_0^S - \rho^S}{\rho_0^S}, \quad \varepsilon = \frac{\rho_0^F - \rho^F}{\rho_0^F}, \end{aligned} \quad (25)$$

where λ^S, μ^S are effective (macroscopic) elasticity parameters of the skeleton, κ is the effective compressibility parameter of the fluid, Q is the coupling constant, δ is the parameter describing changes of porosity due to volume changes of the skeleton and π is the permeability coefficient. All these constants depend parametrically on the initial porosity n_0 .

It is clear that Biot's model describes only isothermal processes. However, within the linear model an extension to cover processes with a varying temperature is straightforward (e.g. see [3]). One has to correct the relations for partial stresses by a contribution of a thermal expansion for each component

$$\mathbf{T}_{therm}^S = -\gamma_T^S (\theta - \theta_0) \mathbf{1}, \quad p_{therm}^F = \gamma_T^F (\theta - \theta_0), \quad (26)$$

where the constants γ_T^S, γ_T^F are related to effective thermal linear expansion coefficients α_T^S, α_T^F by the relations

$$\alpha_T^S = \frac{\rho_0^F \kappa \gamma_T^S - Q / (\rho_0^F \kappa) \gamma_T^F}{3 K^S \rho_0^F \kappa - Q^2}, \quad \alpha_T^F = \frac{K^S \gamma_T^F - Q / K^S \gamma_T^S}{3 K^S \rho_0^F \kappa - Q^2}, \quad K^S = \lambda^S + \frac{2}{3} \mu^S, \quad (27)$$

while the volume changes of the skeleton and of the fluid are given by the relations

$$\begin{aligned} e &= \frac{1}{3K^S} \left(1 + \frac{Q^2}{K^S \rho_0^F \kappa - Q^2} \right) \text{tr}(\mathbf{T}^S - \mathbf{T}_0^S) + \frac{Q}{K^S \rho_0^F \kappa - Q^2} (p^F - p_0^F) + 3\alpha_T^S (\theta - \theta_0), \\ \varepsilon &= -\frac{K^S}{K^S \rho_0^F \kappa - Q^2} (p^F - p_0^F) - \frac{Q}{3(K^S \rho_0^F \kappa - Q^2)} \text{tr}(\mathbf{T}^S - \mathbf{T}_0^S) + 3\alpha_T^F (\theta - \theta_0), \end{aligned} \quad (28)$$

which easily follow from (25) and (26). These relations play an important role by the identification of material constants for granular materials by means of the so-called Gassmann relations (e.g. [14]), which describe their dependence on the initial porosity n_0 . Clearly, in the particular case of lack of coupling between components described by the constant Q (the so-called simple mixtures which follow from the second law of thermodynamics when the dependence on the gradient of porosity is not accounted for) these relations have the form analogous to relations of thermoelasticity

$$e = \frac{\text{tr}(\mathbf{T}^S - \mathbf{T}_0^S)}{K^S} + 3\alpha_T^S (\theta - \theta_0), \quad \varepsilon = -\frac{p^F - p_0^F}{\rho_0^F \kappa} + 3\alpha_T^F (\theta - \theta_0). \quad (29)$$

In addition, one needs the energy balance equation (23) to describe temperature changes. This extension requires constitutive relations for the internal energy and for the heat flux vector \mathbf{q} . The construction of the constitutive relation for the heat flux vector and of the relation for the permeability coefficient π is not an easy task for porous and granular materials. We present here some issues related to this problem.

The heat (thermal) conductivity of porous materials, in contrast to single component continua should be constructed by a combination of heat conductivities of components. The heat flux vector \mathbf{q} for a two-component porous materials in the case of the local thermodynamical equilibrium (a single temperature) can be written in the form

$$\mathbf{q} = -\mathbf{k}_\theta \text{grad } \theta + \mathbf{k}_v (\mathbf{v}^F - \mathbf{v}^S). \quad (30)$$

Obviously, the first contribution is due to the conduction (Fourier) and the second one due to convection (diffusion). The material parameters heat (thermal) conductivity tensor \mathbf{k}_θ and the thermodiffusion tensor \mathbf{k}_v must follow from the properties of the components as well as their interactions. For macroscopically isotropic materials these tensors reduce to two material constants $\mathbf{k}_\theta = \lambda_\theta \mathbf{1}$ and $\mathbf{k}_v = \lambda_v \mathbf{1}$, where $\mathbf{1}$ is a unit tensor for Cartesian coordinates.

In many cases of classical fluid mixtures these coefficients can be calculated by means of the kinetic theory.

For immiscible mixtures such a procedure is not available. There are some attempts to derive an average thermal conductivity (e.g [5]) by means of the volume averaging which amounts to the integration over the Representative Elementary Volume (*REV*). For a two-component porous medium this procedure yields the following relation

$$\mathbf{k}_\theta = (n\lambda_\theta^F + (1 - n)\lambda_\theta^S) \mathbf{1} + \frac{\lambda_\theta^F - \lambda_\theta^S}{\text{vol}(\text{REV})} \int_A \mathbf{n} \otimes \mathbf{b}^F dA, \quad (31)$$

where $\lambda_\theta^F, \lambda_\theta^S$ are the true thermal conductivities of the fluid and of the skeleton, respectively, $\text{vol}(\text{REV})$ is the volume of *REV*, A is the surface of contact between the skeleton and the fluid within *REV* and \mathbf{b}^F is a material structural parameter proportional to the normal vector \mathbf{n} of the surface A for isotropic materials. Not much has been done to determine this parameter. Some remarks on its determination can be found in the book [5].

In practical applications such as freezing of soils where more than two components appear (e.g. solid matrix, ice nuclei, water) in the system one uses empirical relations verified in field experiments. For the thermal conductivity it is often assumed that it is a geometrical mean of partial conductivities of the skeleton and of a fluid component in the channels

$$\lambda_\theta = \prod_{i=1}^{A+1} (\lambda_{\theta i})^{n_i}, \quad (32)$$

where $\lambda_{\theta i}$ are the thermal conductivities of the components and n_i their volume contributions. For instance, for the clay quoted in the Table below by the full saturation with water and the porosity $n_0 = 0.25$ we would obtain a value between 0.16 and 0.88 which is far away from the results indicated in the last row of the Table.

Some modifications of this relation were introduced by Ø. Johansen in 1975 and the nomograms (moisture content, or saturation vs. mass density vs. thermal conductivity; moisture is the water content in the gas component in channels) constructed by means of his relation are frequently used in geophysics. Another approach, called Wiener additivity theory, proposes a relation with a free material parameter α which is equal to zero for an arithmetic average, it is infinite for harmonic average and it is 0.5 for the Maxwell additivity principle. However, a good theoretical model of the heat conductivity for immiscible mixtures is still missing. On the other hand, experimental methods for measuring this coefficient in granular materials, in particular in soils, have been recently successfully developed. Such devices as a non-steady-state probe for thermal conductivity measurement or a heat flux sensor enable studies of building envelope thermal resistance, the effect of fire and flames or properties of soils near the point of freezing.

The second contribution to the heat flux (30) describes the flux of energy caused by the diffusion. For many problems of civil engineering it may be neglected due to a very small diffusion velocity in structural materials such as concrete or natural rocks. Typically, the flux caused by the conduction in such structures (e.g. masonry) is of the order of 50 [$\text{W}\cdot\text{m}^{-2}$]. As the coefficient of thermodiffusion is of the order of the energy density $\rho^F \varepsilon^F$, for water it would be approximately (in temperature 293 K) 250 [$\text{kg}\cdot\text{m}^{-3}$] \cdot 4.1813.

$10^{-3} [\text{MJ}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}]\cdot 293 \text{ K} = 306.28 \cdot 10^6 [\text{J}\cdot\text{m}^{-3}]$ in materials of porosity $n_0 = 0.25$. Consequently, by the velocity of diffusion $10^{-7} [\text{m}\cdot\text{s}^{-1}]$ (this is, for instance, the velocity of contaminant in the ground water appearing in nature) this contribution of convection would be of the same order of magnitude as the contribution of conduction. For higher velocities it would dominate in the energy flux. This may be very well the case for civil engineering constructions with an essential amount of the moisture transport and it is, certainly, the case, for instance, by the transpiration cooling devices (e.g. for cooling leading edges and nose of rockets such as SpaceLiner or turbine blades with thin trailing edges).

Table: Mass density ρ , heat (thermal) conductivity λ_θ and specific heat c_v .

For comparison, under standard conditions
(temperature $\theta = 293.15 \text{ K}$, pressure $p = 101.325 \text{ kPa}$):

water $\rho = 998.2071 [\text{kg}\cdot\text{m}^{-3}]$, $\lambda_\theta = 0.6 [\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}]$, $c_v = 4.1813 [\text{MJ}\cdot\text{m}^{-3}\cdot\text{K}^{-1}]$;
air $\rho = 1.204 [\text{kg}\cdot\text{m}^{-3}]$, $\lambda_\theta = 0.025 [\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}]$, $c_v = 0.00121 [\text{MJ}\cdot\text{m}^{-3}\cdot\text{K}^{-1}]$.

rock/soil	density $10^3[\text{kg}\cdot\text{m}^{-3}]$	heat conductivity $[\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}]$	specific heat $[\text{MJ}\cdot\text{m}^{-3}\cdot\text{K}^{-1}]$
basalt	2.6 - 3.2	1.3 - 2.3	2.3 - 2.6
granite	2.4 - 3.0	2.1 - 4.1	2.1 - 3.0
marble	2.5 - 2.8	1.3- 3.1	2.0
shale	2.7	1.5 - 2.6	2.2 -2.5
halite (rock salt)	2.1 - 2.2	5.3 - 6.4	1.2
sandstone	2.1 - 2.7	1.3 - 5.1	1.6 - 2.8
gravel (wet)	2.7 - 2.8	0.4 - 0.8	1.4 - 1.6
gravel (saturated)	2.7	1.8	2.4
sand (dry)	2.6 - 2.7	0.3 - 0.8	1.3 - 1.6
sand (saturated)	2.6 - 2.7	1.7 - 5.0	2.2 - 2.9
clay (dry)		0.1 - 1.0	1.5 - 1.6
clay (wet)		0.9 - 2.3	1.6 - 3.4

The permeability. The source of momentum $\hat{\mathbf{p}}$ in relation (25) was considered for the first time by P. G. Darcy. He introduced a relation between the pressure gradient and the diffusion velocity. In his formulation it was a linear relation $q = k \cdot (\varphi_1 - \varphi_2) / L$ between the so-called hydraulic gradient $(\varphi_1 - \varphi_2) / L$ and the volumetric discharge q , the first proportional to the pressure difference and the second to the relative velocity. The coefficient k is constant and called hydraulic conductivity. First with the development of the theory of immiscible mixtures it has been shown that Darcy's law is a particular case of the partial momentum balance with a linear constitutive law for the momentum source. The permeability coefficient π is then inversely proportional to the hydraulic conductivity $\pi = g\rho^F k^{-1}$, where g is the gravity of the Earth. Those simple relations have been subsequently developed in order to reveal a physical insight of the phenomenon of resistance to the diffusion. The first proposition related the hydraulic conductivity to the viscosity of the fluid in the channels. The constant k was written in the form $k = \kappa g\rho^F n^{-1} \mu^{-1}$, where μ is the dynamic viscosity. It is claimed that κ , the permeability,

describes only the properties of a dry skeleton while the presence of the fluid in the channels is accounted for by the viscosity. In the next step done by J. Kozeny (1929) a dependence of permeability on the so-called tortuosity was introduced. The notion of tortuosity is connected with the curvy character of streamlines in porous materials. In a given direction it is a ratio of the length of the streamline between two near points to the distance of these points. Consequently, the tortuosity is always greater than one. Originally, Kozeny's relation was linear with respect to the tortuosity. P. C. Carman has shown in 1937 that it must be quadratic. Further, the relation of tortuosity to the geometry of the microstructure of porous media was investigated by J. Bear. It has been found that this quantity is a tensor of the second grade which reduces to a single scalar for isotropic media. Consequently, the relation for the momentum source (25) was generalized to the form $\hat{\mathbf{p}}^S = \pi_{ij} (v_j^F - v_j^S) \mathbf{e}_i$.

Within the frame of a linear thermoporoplasticity the momentum source contribution can be also linearly dependent on the temperature gradient. This type of relations are considered for mixtures of fluids in which Onsager relations are used for the nonequilibrium contributions of the relative velocity (diffusion) and the temperature gradient (thermal convection). Such considerations are still missing in the theory of porous media.

4 Two challenges

We demonstrate on two examples problems arising in the stress and flow analysis in thermomechanics of porous materials. These two problems have only partial solutions.

Let us begin with the **transpiration cooling**. In principle, in technologies one can distinguish three types of cooling: by a film, by a convection and by a transpiration. The latter appears, of course, in many natural biological processes as well but it became recently also an efficient method of cooling in some extreme technological conditions. In this process a coolant is coming from a reservoir through porous walls in the direction of a hot gas side. In passing the porous medium the coolant absorbs the energy transferred in the wall by conduction. In applications this process reaches after a certain time a steady state. The coolant forms a film on the hot gas side which absorbs the convective heat energy transfer and, consequently, reduces the heat transferred to the wall. The coolant on the surface moves downstream by the momentum of the hot gas flow. This method of cooling is used, for instance, for turbine blades which may operate in much higher turbine inlet temperatures. One of the spectacular applications is cooling of leading edges of hypersonic vehicles. For instance, in the project SpaceLiner a vehicle is designed to follow the skip trajectories at an altitude of some 75 [km] and with the velocity of 6550 [m/s]. This is the same speed regime as the Space Shuttle but it will fly at lower altitudes. Consequently, it develops higher temperatures which may reach at least 2900 [K] and 2400 [K] on the leading edges and the nose, respectively. These high temperatures are supposed to be reduced by the application of a porous material (Porcelit 170: 91%, Al₂O₃ and 9% SiO₂) which carries liquid water due to capillary forces created by the evaporation on the hot side. This seems to be a feasible solution for the SpaceLiner as the total mass of the orbiter and booster is 235000 [kg] in comparison to 860000 [kg] propellant and app. 9000 [kg] water needed for the cooling.

Various theoretical and experimental problems arise in relation to the design of such

cooling devices. Among theoretical problems one should mention:

1. construction of a model of heat conduction and mechanical behavior (e.g. thermal stresses) of the porous material in the transpiration zone,
2. construction of boundary conditions for a two-component system with different temperatures of the components and open boundaries,
3. solutions (numerical) of various boundary value problems, usually steady state, for various geometries and external conditions for various materials as well as the optimization of the structure.

Modeling is as yet very crude and based on two ordinary differential equations for the one-dimensional steady state partial energy balance for two temperatures: θ^F of the fluid and θ^S of the solid porous matrix (e.g. [9]). They have the form

$$\frac{d\theta_f}{d\eta} = \frac{h'L}{\dot{m}^F c_p} (\theta_s - \theta_f), \quad \frac{d\theta_s}{d\eta} = \frac{\dot{m}^F L}{k_s} \theta_f, \quad (33)$$

where

$$\theta_f = \frac{\theta^F - \theta_i^F}{\theta_w^S - \theta_i^F}, \quad \theta_s = \frac{\theta^S - \theta_i^F}{\theta_w^S - \theta_i^F}, \quad \eta = \frac{x}{L}, \quad \dot{m}^F = \rho^F (v_x^F - v_x^S), \quad (34)$$

and θ_i^F is the temperature of the reservoir, θ_w^S the (constant) temperature of the matrix at the exit, L the length of the one-dimensional system, \dot{m}^F denotes a constant mass rate flow. h' is the so-called heat transfer coefficient for the internal convection, c_p is the specific heat of the fluid and k_s is the effective conductivity of the matrix. Before we discuss solutions of this set of equations let us try to fit them into the scheme of the two-component model presented before in this article. Making the identifications $\rho^F \dot{\mathbf{X}}^F \cdot \mathbf{e}_x = \dot{m}^F$ where \mathbf{e}_x is a unit vector pointing in the direction of x -axis, and $\mathbf{Q}^S = -k_s \text{Grad } \theta^S$, $\hat{\varepsilon}^S = -\hat{\varepsilon}^F = h' (\theta^F - \theta^S)$ we obtain (33)₁ as a rough approximation of (10)₂ and (33)₂ as a rough approximation of (10)₁. Clearly, the fluid must be ideal $\mathbf{T}^F = -p^F \mathbf{1}$ then the differentiation of the partial enthalpy of the fluid $h^F = \varepsilon^F + p^F / \rho^F$ (the partial pressure p^F chosen as a constitutive variable instead of the partial mass density ρ^F) yields the specific heat c_p . Simultaneously, an influence of partial stresses in the skeleton must be entirely neglected. However, the main point in this identification concerns the interpretation of partial temperatures θ^S, θ^F . These are clearly macroscopic smeared out quantities as they enter smeared out energy balance equations (10). On the other hand, both in the boundary conditions as well as in their physical interpretation these temperatures are considered as they were true temperatures of the components. Such quantities as mass, momentum and energy which are all extensive can be averaged over, say, the representative elementary volume (*REV*) by volume integration. Temperatures are not extensive quantities and, consequently, their averaging is much more complex and yields additional contributions which we may call spatial fluctuations (compare some remarks by M. Kaviani [5]).

In addition, we cannot expect that both temperatures are simultaneously measurable and controllable on boundaries. This means that the values of partial temperatures cannot be assumed to be given on a boundary in contrast to the assumption in the work [9]. This problem has been recently approached by J. H. Wang and his coworkers [12]. They have tested five different arbitrarily chosen boundary conditions and by means of a numerical

analysis selected these which, as they claim, fit best the expectations. There is no physical argument supporting this choice. This problem of thermodynamics of multicomponent systems seems to be still open.

It is also clear that the above described model neglects entirely couplings with deformations, thermal stresses and latent heat of phase transformations. The latter problem is connected with an essential energy consumption during evaporation.

The second example which contains essential points of modeling of thermoporous materials is the problem of **freezing and thawing**. This process yields the frost heaving of pavements, the deterioration of concrete from freeze-thaw action, the creation of palsas in regions of discontinuous permafrost, of the great interest by freezing is the durability of water infiltrated materials or the determination of the cooling rates for the food preservation or cryopreservation of organs for transplantation. O. Coussy in his work [4] has listed the main mechanisms appearing in such processes. This work contains also numerous references to particular subjects involved.

The material undergoing cooling below the freezing point is subject to at least six actions:

1. increment of the pore pressure due to the difference of densities (specific volumes) of the liquid water and ice crystals,
2. interfacial effects, surface tension between water and bubbles as well as wetting on surfaces of the solid matrix and ice crystals which govern the crystallization process,
3. drainage of the liquid water,
4. cryo-suction process which drives liquid water to air bubbles,
5. thermomechanical coupling between solid matrix, ice lenses and the liquid water with air bubbles,
6. changes of porosity and permeability due to creation of microcracks (damage) by formation of ice crystals.

The confined water can partially remain liquid in temperatures below the bulk freezing point. This is caused by a depressurizing effect in water near ice crystals and yields the cryo-pumping from warm inner layers to frozen fringe layers. As a consequence the frost heave effect and palsas appear. Hence, the frost heave requires a macroscopic temperature gradient.

The work of Coussy [4] contains a construction of a linear thermoporoelastic model which accounts for the first five actions listed above. For the fields of deformation of the skeleton \mathbf{e}^S , partial pressures in the ice crystals p^C and in the water p^W , energy of interfaces between water and ice crystals U and temperature T field equations are constructed on the basis of linearized partial balance equations. For instance, the constitutive relation for partial stresses in the skeleton as one of the closing relations which replaces relations (25), (26) is as follows

$$\begin{aligned} \mathbf{T}^S = & \mathbf{T}_0^S + \lambda^S e \mathbf{1} + 2\mu^S \mathbf{e}^S + \\ & + \left[b^C \left(p^C - \frac{2}{3}U \right) + b^W \left(p^W - \frac{2}{3}U \right) - \gamma_T^S (\theta - \theta_0) \right] \mathbf{1}, \end{aligned} \quad (35)$$

where the constants b^C, b^W correspond to the splitting of the Biot coupling constant Q between ice crystals and water and the subsequent change of variables from partial volume changes to partial pressures. The full change of porosity $n - n_E$ is assumed in this model to consist of the contribution due to volume changes of the skeleton, ice crystals and water as well a contribution of the degree of saturation S^L . This in turn satisfies a state relation in which the difference of partial pressures $p_c = p^C - p^L$, the so-called capillary pressure, appears (liquid saturation curve). In this relation hysteresis effects, appearing in reality, are neglected. The system of equations is closed by a generalization of Darcy's law. The work does not contain any considerations concerning the distribution of temperature and, consequently, an influence of thermal stresses. Completely ignored is the question of damage through microcracking during freezing. This problem appears in the literature under the heading of the Gurson-Tvergaard-Needleman yield criterion formulated for metals in which microcracking contributes to the brittle damage. The yield function of this model has the following form

$$f_{GTN} = \frac{\sigma_{eq}^2}{\sigma_s^2} + 2q_1n \cosh\left(\frac{1}{2}q_2\frac{T_{kk}^S}{\sigma_s}\right) - 1 - (q_1n)^2, \quad (36)$$

where

$$\sigma_{eq} = \sqrt{\frac{3}{2}T_{ij}^{Sdev}T_{ij}^{Sdev}}, \quad T_{ij}^{Sdev} = T_{ij}^S - \frac{1}{3}T_{kk}^S\delta_{ij}, \quad (37)$$

and σ_s is the yield stress which may consist of two parts: yield stress at the beginning of the damage and the hardening. q_1, q_2 are the material parameters a little bigger than one. Clearly, the first term describes the yield function for the classical von Mises criterion. The most essential part of the above law is the changing porosity which reflects a density of microcracks. This must be described by an evolution law which enters the right hand side of the porosity balance equation [1].

The above remarks indicate that the model of freezing-thawing processes in porous media is still in the very early stage of development. However, in contrast to the first problem indicated above all ingredients of the model are already known and they require only a systematic exposition.

5 Concluding remarks

Modeling of thermoporoelastic materials is still a very much open subject of research. This concerns the thermodynamical foundations of various specific models as well as the formulation of boundary conditions and solutions of boundary value problems. Since some fifty years it was the main concern to investigate the propagation of acoustic waves in such materials under isothermal conditions with very little attention paid to such problems as distribution of stresses and deformations, damage problems or distribution of temperatures.

We briefly recall the questions which are still very much open for the further research

- thermodynamical foundations of a model of immiscible mixtures with multiple temperatures; in particular – formulation of boundary conditions for such a model,

- extension of a linear thermoporoelastic model on at least nonlinearities following from the dependence of the material parameters on the changing porosity and the temperature; such dependencies are at the present accounted for by iteration procedures, i.e. processes with small deviations from an initial state,
- construction of effective macroscopic parameters, particularly describing fluxes of momentum and energy: in particular: construction of heat conductivities, coupling thermal parameters with diffusion, permeabilities,
- construction of evolution laws for mass production by such phase transformations as freezing and evaporation,
- construction of a liquid saturation curve with hysteresis.
- analysis of thermal stresses in processes at high temperatures (e.g. in porous shields for transpiration cooling).

It is clear from the examples mentioned above that the research in all these directions is highly desired.

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