

Nonlinear thermomechanics of immiscible mixture

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1. Nonlinear thermomechanics of immiscible mixture

1.1. Introduction

Thermodynamic modelling of immiscible mixtures began with works of R. M. Bowen [1, 2]. These fundamental works as well as numerous original papers of Bowen contain very important results on the structure of nonlinear constitutive relations for mixtures in which at least one of the components is an elastic solid. However, in spite of its path breaking character this approach contains two flaws which went unnoticed in various contributions to this macroscopic model of diffusion processes in porous materials.

First of all, R. M. Bowen introduces a Lagrangian description in a way which is obviously erroneous. For instance, the formula (1.1.1) in [1] which is supposed to describe the motion of an arbitrary component α , has the following form (in the original notation of R. M. Bowen)

$$\mathbf{x} = \chi_{\alpha}(\mathbf{X}_{\alpha}, t), \quad (1)$$

where “ \mathbf{X}_{α} is the position of a particle of the α th body in its reference configuration, t the time, and \mathbf{x} the spatial position occupied at the time t by the particle labelled \mathbf{X}_{α} ” [1]. As a consequence, field equations in such a description are not defined on the same space as, for instance, each partial balance of momentum for the component α is defined on the space \mathcal{B}_{α} of points \mathbf{X}_{α} and, even worse, different contributions to those equations describing couplings with other components depend on variables from different spaces \mathcal{B}_{β} , $\beta \neq \alpha$ of points \mathbf{X}_{β} . In order to obtain a proper mathematical formulation one has to transform them to the Eulerian description losing all advantages of the Lagrangian description. In addition, equal smoothness of functions χ_{α} is necessary and, in addition, $\chi_{\alpha}(\mathcal{B}_{\alpha}, t) = \chi_{\beta}(\mathcal{B}_{\beta}, t)$ for all α, β . This fault has been later on repeated by many authors. It is even worse when we choose the same reference configuration, say, \mathcal{B}_0 , for all components as this yields particles

of different components to lie very far apart in any current configuration. Then, in the Eulerian description, particles interact with each other on long distances which means that the theory should be nonlocal. The reason for the fault not being noticed by R. M. Bowen is most likely related to the fact that his papers are primarily devoted to the construction of constitutive relations for homogeneous materials and nonlinear field equations are not even quoted. All boundary-value problems considered by Bowen such as propagation of acoustic waves are linearized and then the Eulerian and Lagrangian description are identical.

The second fault is related to the form of the second law of thermodynamics. It is based on the entropy inequality (e.g. relation (5A.1.8) in [2])

$$\sum_{\alpha=1}^N \left(\rho_{\alpha} \eta_{\alpha} + \operatorname{div} \left(\mathbf{q}_{\alpha} / \theta_{\alpha} \right) - \rho_{\alpha} r_{\alpha} / \theta_{\alpha} \right) \geq 0, \quad (2)$$

in which the vector of the entropy flux is assumed to be dependent only on partial heat flux vectors and partial temperatures. It does not contain terms dependent on relative velocities which appear in a natural way in all mixture theories. Such extended relations were introduced by I. Müller [6]. In addition, there exist numerous unsolved problems following from different temperatures of components. They are not continuous across any material surface and, consequently, they are not measurable. This means that classical boundary problems of heat conduction cannot be formulated. In the case of a single temperature field this problem is solved by the assumption on the existence of the so-called ideal walls (e.g. [7, 11, 13]). Attempts to extend this notion on multitemperature fields of many components are not yet successful.

In this note, we present a way in which the faults appearing in Bowen's papers can be corrected. We show how to introduce the Lagrangian description for immiscible mixtures in a proper way and we discuss some constitutive issues mentioned already by R. M. Bowen but not elaborated enough. Many important details of the construction of nonlinear models have been established in a very recent research and they yield essential deepening of Bowen's models. This concerns, in particular, a corrected structure of the second law of thermodynamics for multicomponent systems with a single absolute temperature field θ . In contrast to works of R. M. Bowen, we also use a specific form of the objective relation for relative accelerations. For instance, in the article [2]

Bowen accounts for the objectivity requirements making the assumption that the skeleton is viscoelastic. This assumption can be avoided by shifting an appropriate dependence on the rate of deformation gradient to the nonlinear definition of the relative acceleration.

1.2. Lagrangian description

Description of motion of multicomponent systems can be constructed in many different ways. In the case of a system whose one component is solid one can use either the Eulerian description of motion or one of Lagrangian descriptions. In the first case, the motion is described by fields of partial velocities $\mathbf{v}^\alpha(\mathbf{x}, t)$ of components given as functions of points $\mathbf{x} \in \mathfrak{R}^3$ in current configurations and time t . In principle, under appropriate smoothness assumptions these functions can be integrated – it is the problem of the solution of the set of nonlinear ordinary differential equations

$$\frac{d\mathbf{x}}{dt} = \mathbf{v}^\alpha(\mathbf{x}, t), \quad \mathbf{x}(t=0) = \mathbf{X}^\alpha, \quad \alpha = 1, \dots, N. \quad (3)$$

A unique global solution exists always and one obtains the set of trajectories for particles \mathbf{X}^α of components (initial positions of particles of the α -component). This step is usually not doable analytically and, therefore, ignored in practical applications. All other fields, mass densities, deformations, diffusion velocities, partial stresses, temperature distribution, etc., one obtains without an explicit knowledge of trajectories, i.e. solutions of the set (3).

One can choose as well a reference configuration of a chosen component to describe the motion of all other components. In the case of porous materials, it is usually a configuration of the solid component (skeleton) and the motion of all other components is described relative to the skeleton. However, there are cases, for instance suspensions, in which a reference configuration of the fluid component is more convenient than this of the solid phase (suspended solid granule). We present here in some details the method of Lagrangian description with respect to the reference configuration of the skeleton.

As in a single component continuum it is assumed that, for a chosen reference configuration \mathcal{B}_0 the motion is described by the diffeomorphism

$$\mathbf{x} = \mathbf{f}^S(\mathbf{X}, t), \quad \mathbf{X} \in \mathcal{B}_0 \quad (4)$$

which specifies the position \mathbf{x} of an arbitrary material point of the skeleton \mathbf{X} at the instant of time t . As usual, its gradient defines the deformation gradient of the skeleton \mathbf{F}^S , and its time derivatives the velocity of the skeleton \mathbf{x}'^S and the acceleration of the skeleton \mathbf{x}''^S

$$\mathbf{F}^S = \text{Grad} \mathbf{f}^S, \quad \mathbf{x}'^S = \frac{\partial \mathbf{f}^S}{\partial t}, \quad \mathbf{x}''^S = \frac{\partial \mathbf{x}'^S}{\partial t}, \quad \det \mathbf{F}^S \neq 0. \quad (5)$$

The function of motion \mathbf{f}^S is assumed to be almost everywhere twice differentiable with respect to spatial and temporal variables.

Note the difference in the notation in comparison to Bowen's work on this subject.

The choice of the skeleton as the reference of the motion can be interpreted that the motion of fluid components filling the pores of the skeleton takes place not in the usual Euclidean space but in a special deformable space made available by the skeleton, or rather by its channels. We introduce the description of this motion by means of the usual Eulerian description and the so-called pull-back operation [5]. It means that the partial mass densities ρ^α , partial velocities \mathbf{v}^α and all other partial quantities of the α -component, $\alpha = 1, \dots, A$, are functions of the current position, \mathbf{x} , and the time, t . As the function of motion of the skeleton is invertible, we can define the following functions on the reference configuration \mathcal{B}_0

$$\begin{aligned} \rho^\alpha &= \rho^\alpha(\mathbf{f}^S(\mathbf{X}, t), t) = \rho^\alpha(\mathbf{X}, t), \\ \mathbf{x}'^\alpha &= \mathbf{v}^\alpha(\mathbf{f}^S(\mathbf{X}, t), t) = \mathbf{x}'^\alpha(\mathbf{X}, t), \quad \alpha = 1, \dots, A, \end{aligned} \quad (6)$$

and similarly for all other quantities describing fluid components. In order to make the presentation as simple as possible we are here a little sloppy with the denotation of functions.

As we see in the next Section, the differences of partial velocities of fluid components and of the velocity of the skeleton have a particular importance.

They describe the diffusion in the body. Projected on the reference configuration of the skeleton they have the form

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

and these objects are called Lagrangian velocities [11]. They are objective, i.e. invariant with respect to the rigid body motion defined by the relation

$$\mathbf{x}^* = \mathbf{x}_0(t) + \mathbf{O}(t)\mathbf{x}, \quad \mathbf{O}^T(t) = \mathbf{O}^{-1}(t), \quad (8)$$

where $\mathbf{x}_0(t)$, $\mathbf{O}(t)$ are arbitrary functions of time. As objective quantities they can be used as constitutive variables in thermodynamics of porous materials.

Other quantities which appear in relation to microstructural properties of porous materials are relative accelerations. It is easy to see that the differences $\mathbf{x}''^\alpha - \mathbf{x}''^S$ are not objective. However, there are many ways of introducing objects which contain the difference of accelerations as the main contribution and simultaneously are invariant with respect to the rigid body motion. The simplest definition of this art was introduced in the work [12] and, for many fluid components, it has the form

$$\mathbf{a}_r^\alpha = \mathbf{a}_r^\alpha(\mathbf{X}, t) = (\mathbf{x}''^\alpha - \mathbf{x}''^S) - (1 - z^\alpha) \mathbf{X}'^\alpha \cdot \text{Grad} \mathbf{x}'^\alpha - z^\alpha \mathbf{X}'^\alpha \cdot \text{Grad} \mathbf{x}'^S, \quad (9)$$

where z^α are arbitrary constitutive scalar parameters. It is easy to observe the similarity of this definition to the Oldroyd definition of the acceleration in a single component continuum

$$\mathbf{a} = \mathbf{a}(\mathbf{x}, t) = \ddot{\mathbf{x}} = \frac{\partial \mathbf{v}}{\partial t} + \mathbf{L}^T \mathbf{v}, \quad \mathbf{L} = \text{grad} \mathbf{v}. \quad (10)$$

However, instead of the Eulerian description in Oldroyd's definition, we have in the present case the description of motion with respect to the reference configuration of the skeleton. In this configuration all fluid components are "moving" as this reference configuration was the space of motion. These motions are, obviously, defined by the pull-back operation.

In the above relations as well as in the rest of the paper the operators Grad, Div are referring to the Lagrangian coordinates of the skeleton and the operators grad, div are referring to the Eulerian description.

1.3. Balance laws

As in the case of a single component continuum the balance laws form the foundation of continuous modelling of porous materials. These laws specify time changes of fields of mass densities, momentum densities, energy densities, entropy densities and in some models, some additional microstructural quantities such as the porosity. The basic notion in the construction of such laws is the notion of material domains. In the case of a single body these are certain measurable subsets of the body. In models in which the body is identified with its reference configuration \mathcal{B}_0 , and this is the case for the skeleton in the above chosen Lagrangian description, these subsets satisfy axioms introduced to continuum mechanics by M. E. Gurtin, W. Noll, W. O. Williams (e.g. [3]) and presented by C. Truesdell [8] (see also: [10, 9, 4]). For such a material subbody $\mathcal{P}^S \subset \mathcal{B}_0$ the balance law for the skeleton has the general form

$$\frac{d}{dt} \int_{\mathcal{P}^S} \rho^S \varphi^S dV = \oint_{\partial \mathcal{P}^S} \boldsymbol{\Psi}^S \cdot \mathbf{N} dS + \int_{\mathcal{P}^S} \hat{\varphi}^S dV, \quad (11)$$

where $\partial \mathcal{P}^S$ is the boundary of the subbody \mathcal{P}^S and \mathbf{N} is the unit outward normal vector on this surface. φ^S is the specific density – it may be scalar, vector or tensor quantity, which satisfies the balance equation. It is equal to 1 for the mass density of the skeleton, \mathbf{x}'^S for the momentum balance, $\varepsilon^S + \frac{1}{2} \mathbf{x}'^S \cdot \mathbf{x}'^S$ for the energy balance, η^S for the entropy balance. $\boldsymbol{\Psi}^S$ is the nonconvective flux, and $\hat{\varphi}^S$ is the additive combination of external supplies and sources for the skeleton. Obviously, in the Lagrangian description with respect to the skeleton, the left-hand side of this relation can be written in the form

$$\frac{d}{dt} \int_{\mathcal{P}} \rho^S \varphi^S dV = \int_{\mathcal{P}} \frac{\partial (\rho^S \varphi^S)}{\partial t} dV. \quad (12)$$

This is not the case any more for balance equations of fluid components. Material subbodies for the α -component are defined in current configurations by the velocity fields $\mathbf{v}^\alpha(\mathbf{x}, t)$. The domain $\mathcal{P}_t^\alpha \subset \mathbf{f}^S(\mathcal{B}_0, t) \subset \mathfrak{R}^3$ in those configurations is material for this component if its boundary $\partial \mathcal{P}_t^\alpha$ moves with the velocity $\mathbf{v}^\alpha(\mathbf{x}, t)$. Consequently, its image in the reference configuration defined by the mapping $\mathcal{P}^\alpha(t) = \mathbf{f}^{S-1}(\mathcal{P}_t^\alpha, t)$ has the kinematics determined by the Lagrangian velocity $\mathbf{X}'^\alpha(\mathbf{X}, t)$, i.e. its boundary points are moving with this

Lagrangian velocity. Obviously, they are not material with respect to the skeleton in which case they would have the zero velocity of boundary points. The balance equation for the α -component possesses the same structure as in the case of the skeleton

$$\frac{d}{dt} \int_{\mathcal{P}^\alpha(t)} \rho^\alpha \varphi^\alpha dV = \oint_{\partial \mathcal{P}^\alpha(t)} \boldsymbol{\Psi}^\alpha \cdot \mathbf{N} dS + \int_{\mathcal{P}^\alpha} \hat{\boldsymbol{\varphi}}^\alpha dV, \quad (13)$$

but the domains of integration are now functions of time, i.e.

$$\begin{aligned} & \frac{d}{dt} \int_{\mathcal{P}^\alpha(t)} \rho^\alpha \varphi^\alpha dV = \\ & = \int_{\mathcal{P}^\alpha(t)} \frac{\partial(\rho^\alpha \varphi^\alpha)}{\partial t} dV + \oint_{\partial \mathcal{P}^\alpha(t)} \rho^\alpha \varphi^\alpha \mathbf{X}'^\alpha \cdot \mathbf{N} dS. \end{aligned} \quad (14)$$

The above global relations yield local balance laws in regular points and jump conditions on singular surfaces. We quote here only the set of three fundamental balance equations for the skeleton and for fluid components. They have the following form

- partial balance equations of mass

$$\frac{\partial \rho^s}{\partial t} = \hat{\rho}^s, \quad \frac{\partial \rho^\alpha}{\partial t} + \text{Div}(\rho^\alpha \mathbf{X}'^\alpha) = \hat{\rho}^\alpha, \quad (15)$$

- partial balance equations of momentum

$$\begin{aligned} & \frac{\partial(\rho^s \mathbf{x}'^s)}{\partial t} - \text{Div} \mathbf{P}^s = \hat{\mathbf{p}}^s + \rho^s \mathbf{b}^s, \\ & \frac{\partial(\rho^\alpha \mathbf{x}'^\alpha)}{\partial t} + \text{Div}(\rho^\alpha \mathbf{x}'^\alpha \otimes \mathbf{X}'^\alpha - \mathbf{P}^\alpha) = \hat{\mathbf{p}}^\alpha + \rho^\alpha \mathbf{b}^\alpha, \end{aligned} \quad (16)$$

- partial balance equations of energy

$$\begin{aligned}
& \frac{\partial \left(\rho^s \left(\varepsilon^s + \frac{1}{2} \mathbf{x}'^s \cdot \mathbf{x}'^s \right) \right)}{\partial t} + \text{Div} \left(\mathbf{Q}^s - \mathbf{P}^{sT} \mathbf{x}'^s \right) = \\
& = \hat{\varepsilon}^s + \rho^s \mathbf{x}'^s \cdot \mathbf{b}^s + \rho^s r^s, \\
& \\
& \frac{\partial \left(\rho^\alpha \left(\varepsilon^\alpha + \frac{1}{2} \mathbf{x}'^\alpha \cdot \mathbf{x}'^\alpha \right) \right)}{\partial t} + \\
& + \text{Div} \left(\rho^\alpha \left(\varepsilon^\alpha + \frac{1}{2} \mathbf{x}'^\alpha \cdot \mathbf{x}'^\alpha \right) \mathbf{X}'^\alpha + \mathbf{Q}^\alpha - \mathbf{P}^{\alpha T} \mathbf{x}'^\alpha \right) = \\
& = \hat{\varepsilon}^\alpha + \rho^\alpha \mathbf{x}'^\alpha \cdot \mathbf{b}^\alpha + \rho^\alpha r^\alpha.
\end{aligned} \tag{17}$$

Hence, as could be expected, balance equations for the skeleton have the form similar to the case of Lagrangian description of a single continuum. \mathbf{P}^s denotes the partial Piola-Kirchhoff stress tensor in the skeleton, ε^s is the partial specific internal energy of the skeleton, \mathbf{Q}^s is the partial heat flux in the skeleton, \mathbf{b}^s, r^s is the body force of the skeleton (it may include forces appearing in the case of a noninertial frame of reference) and the partial energy radiation, respectively. As always in the theory of mixture, there appear interaction forces in the form of mass source $\hat{\rho}^s$, momentum source $\hat{\mathbf{p}}^s$ and energy source $\hat{\varepsilon}^s$.

However, balance equations for fluid components contain not only contributions analogous to those of the skeleton but additionally convective terms. They describe additional fluxes created by the fact that material surfaces for the skeleton are not identical with material surfaces of fluids. Fluid components flow through material surfaces of the skeleton with the Lagrangian velocity carrying partial mass, momentum and energy of these components. These contributions are missing in works of Bowen as, in his formulation, each contribution of a particular component to partial balance laws is written in relation to its own reference configuration and its own notion of material surfaces. This is, of course, physically and mathematically erroneous.

As usual in the continuous theory of mixtures proposed by C. Truesdell it is assumed that the bulk conservation laws are satisfied. For mass, momentum and energy they have the following form

$$\hat{\rho}^s + \sum_{\alpha=1}^A \hat{\rho}^\alpha = 0, \quad \hat{\mathbf{p}}^s + \sum_{\alpha=1}^A \hat{\mathbf{p}}^\alpha = 0, \quad \hat{\varepsilon}^s + \sum_{\alpha=1}^A \hat{\varepsilon}^\alpha = 0. \tag{18}$$

These restrictions yield local conservation laws for bulk quantities which we shall not present in this note (compare [14]).

1.4. Entropy inequality

The second law of thermodynamics is formulated in the theory of mixtures as a condition imposed on constitutive relations by the so-called entropy inequality. The formulation of this inequality requires the formulation of balance laws for partial entropies. As in the cases discussed in the previous Section, we have in the Lagrangian formulation with respect to the skeleton the following set of relations

$$\begin{aligned} \frac{\partial(\rho^s \eta^s)}{\partial t} + \text{Div} \mathbf{H}^s &= \rho^s s^s + \hat{\eta}^s, \\ \frac{\partial(\rho^\alpha \eta^\alpha)}{\partial t} + \text{Div}(\rho^\alpha \eta^\alpha \mathbf{X}'^\alpha + \mathbf{H}^\alpha) &= \rho^\alpha s^\alpha + \hat{\eta}^\alpha, \end{aligned} \quad (19)$$

where η^s, η^α are specific partial entropies, $\mathbf{H}^s, \mathbf{H}^\alpha$ are partial nonconvective fluxes of entropy, s^s, s^α are specific entropy supplies and $\hat{\eta}^s, \hat{\eta}^\alpha$ are partial entropy sources. Fluxes of entropy were introduced by I. Müller as constitutive quantities (e.g. [6, 7]). In the theory of single continuum the single entropy flux is proportional to the heat flux and the coefficient – coldness – is equal to the inverse of the absolute temperature. In the theory of mixtures with the common temperature of components it is often assumed that the partial entropy fluxes and heat fluxes satisfy the analogous relations. However the total flux in the bulk entropy balance relation contains additional contributions related to the diffusion. Certainly, it is also the case for porous materials. The addition of partial balance laws of entropy yields

$$\frac{\partial(\rho \eta)}{\partial t} + \text{Div} \left(\mathbf{H}^s + \sum (\rho^\alpha \eta^\alpha \mathbf{X}'^\alpha + \mathbf{H}^\alpha) \right) = \rho s + \hat{\eta}, \quad (20)$$

where

$$\begin{aligned}\rho &= \rho^s + \sum_{\alpha=1}^A \rho^\alpha, & \rho\eta &= \rho^s \eta^s + \sum_{\alpha=1}^A \rho^\alpha \eta^\alpha, \\ \rho s &= \rho^s s^s + \sum_{\alpha=1}^A \rho^\alpha s^\alpha, & \hat{\eta} &= \hat{\eta}^s + \sum_{\alpha=1}^A \hat{\eta}^\alpha.\end{aligned}\quad (21)$$

The second law of thermodynamics has then the following form: for all admissible thermodynamic processes (i.e. all solutions of field equations) the entropy production must be nonnegative, i.e.

$$\hat{\eta} \geq 0. \quad (22)$$

This restriction yields the entropy inequality

$$\frac{\partial(\rho\eta)}{\partial t} + \text{Div} \left(\mathbf{H}^s + \sum_{\alpha=1}^A (\rho^\alpha \eta^\alpha \mathbf{X}'^\alpha + \mathbf{H}^\alpha) \right) \geq 0, \quad (23)$$

in which the entropy supply was neglected as an external agent which means that it can be switched off in the process of evaluation of the entropy inequality.

Neither in the case of the common temperature θ of all components nor in the case of a multitemperature model the assumption

$$\mathbf{H}^s = \frac{\mathbf{Q}^s}{\theta^s}, \quad \mathbf{H}^\alpha = \frac{\mathbf{Q}^\alpha}{\theta^\alpha}, \quad \alpha = 1, \dots, A, \quad (24)$$

where θ^s, θ^α are absolute temperatures of components, incidentally – not defined by Bowen for the multitemperature model, the entropy inequality (23) would be identical with this of R. M. Bowen (5A.1.11) written in his formulation for immiscible mixtures with different reference configurations of components [2]. The missing terms in convective fluxes of the energy and entropy are the main reason for this fault. Consequently, at least a dependence on diffusion velocities in constitutive relations obtained by Bowen is wrong. An example of the model of immiscible mixture in which a proper form of the entropy inequality is evaluated is presented in details, for instance, in the works [12, 13, 14]. In the next Section we illustrate those results by a few examples.

1.5. Example of constitutive relations

In order to demonstrate some consequences of the Lagrangian formulation of thermodynamics presented in this note, we quote here a few representative results for a particular nonlinear model of porous media. This model contains fully nonlinear field equations for the following fields

$$\{\rho^S, \rho^\alpha, \mathbf{x}'^S, \mathbf{x}'^\alpha, \mathbf{F}^S, n, \theta\}, \quad (25)$$

where n, θ are fields of porosity and temperature, respectively. Clearly, we do not introduce the function of motion \mathbf{f}^S as a field but we require its existence. It means that fields (25) must satisfy the integrability conditions

$$\frac{\partial \mathbf{F}^S}{\partial t} = \text{Grad} \mathbf{x}'^S, \quad \text{Grad} \mathbf{F}^S = (\text{Grad} \mathbf{F}^S)^T, \quad (26)$$

where the second relation means that the gradient of the deformation gradient \mathbf{F}^S must be symmetric with respect to the second and third index in Cartesian coordinates.

It is the standard strategy of continuum thermodynamics to construct field equations for fields (25) by means of the assumption that quantities appearing in balance laws which are not explicit functions of the fields and their derivatives must be given by constitutive relations. This is the so-called closure problem. In models with hereditary properties these constitutive relations are functionals on the history of fields and their derivatives. In some models these hereditary functionals are replaced by evolution equations. This is, for instance, the case with the porosity equation. R. M. Bowen proposed for this field an evolution equation. The analysis of a linear Biot model of porous materials indicates an influence of diffusion on changes of porosity which resulted in the proposition of a balance equation of porosity [11]. However, in contrast to standard balance laws this equation does not require additional boundary conditions.

For the model of poroelastic materials with the single field of temperature the set of constitutive variables appearing in constitutive relations is as follows (e.g. [12, 13, 14])

$$\mathcal{C} = \{\rho^S, \rho^\alpha, \mathbf{F}^S, \mathbf{X}'^\alpha, \mathbf{a}_r^\alpha, n, \text{Grad} n, \theta, \text{Grad} \theta\} \quad (27)$$

A few remarks on this choice are appropriate. The field of the mass density of skeleton ρ^S appears among fields and constitutive variables only in the case when there is a mass exchange between components. Then the mass source in equation (15)₁ is different from zero and this partial mass density changes in time. Otherwise it is a constant and can be skipped in the lists (25) and (27). Otherwise we need an additional field, an internal variable, describing the mass exchange. It may be the vector of chemical reactions or some other field describing the rate of mass transfer. We shall not discuss this problem in this note and assume that ρ^S is a constant Lagrangian mass density of the skeleton.

The remaining mass densities ρ^α possess a different character. Even if the mass exchange is absent, i.e. all mass sources are zero, these quantities change due to the deformation of fluid components. In contrast to the skeleton whose deformation is measured by the deformation gradient \mathbf{F}^S the fluids in poroelastic materials are macroscopically ideal and their deformations yield only volume changes determined by changes of partial mass densities.

Special role is played by the contribution of the gradient of porosity $\text{Grad}n$. Its presence is necessary for the appearance of certain couplings of partial stresses whose necessity is indicated by linear models (e.g. [14]). In such linear models it yields constitutive relations in which volume changes of fluid components influence partial stresses in the skeleton and, conversely, the volume changes of the skeleton influence partial pressures in fluid components. The lack of this coupling yields the so-called simple mixture model. Its counterpart appears also in the theory of mixture of fluids [7].

A dependence on the relative accelerations \mathbf{a}_r^α was introduced in the linear model by M. A. Biot who claimed that it describes the so-called tortuosity. The tortuosity is a measure of deviations of channels in porous materials from the straight line geometry. This claim was frequently repeated in the literature. However, it can be easily shown that contributions of relative accelerations yield reversible effects [12] while an influence of tortuosity should be irreversible. A detailed discussion of this problem can be found in the forthcoming paper [15]. However, an influence of the relative accelerations and the so-called added mass coefficients is not forbidden by the second law of thermodynamics.

It is also seen in (27) that we assume the temperatures of components to be equal. This means that energy sources $\hat{\mathcal{E}}^S, \hat{\mathcal{E}}^\alpha$ are equal to zero. The reason

for this assumption is the problem of measurability of partial temperatures and, consequently, the problem of formulation of boundary conditions for heat conduction problem. This problem is still unsolved.

Constitutive relations are constructed in the thermodynamic strategy in this way that they automatically satisfy two fundamental principles:

- thermodynamic admissibility,
- objectivity (frame indifference).

As already mentioned, this problem has been discussed by R. M. Bowen as well as in many more recent papers. Examples and further references can be found in [11, 12, 13, 14]. We present here only two special results to illustrate the deviations of modern constitutive models from those constructed by Bowen.

Let us begin with energy balance. In the case of a single temperature only added energy balances, i.e. the energy conservation equation has the bearing. Then one can show (e.g. [13]) that the heat flux vector \mathbf{Q} and the entropy flux \mathbf{H} are related in the following way for the two-component mixture (i.e. $\alpha = F$)

$$\mathbf{H} = \frac{1}{\theta} (\mathbf{Q} - \rho^F \psi^F \mathbf{X}'^F), \quad (28)$$

where ψ^F is the Helmholtz partial free energy function of the fluid component depending on deformations of both components and on the porosity gradient. Consequently, the relations assumed by Bowen in his exploitation of the second law are not appropriate.

The second example concerns the constitutive relations for partial stresses. Again we limit the attention to the two-component case. In such a model with a linear dependence of momentum sources on the relative velocity and relative acceleration

$$\mathbf{F}^{ST} \hat{\mathbf{p}} = \Pi_v \mathbf{X}'^F - \rho_{12} \mathbf{a}_r^F, \quad (29)$$

where Π_v is the so-called permeability coefficient and ρ_{12} is the added mass coefficient. This relation yields the classical Darcy law but not its nonlinear generalizations (e.g. the Forchheimer generalization for turbulent flows). It is also assumed that hereditary effects are not appearing. Otherwise, the law (29) would contain at least some convolution integrals reflecting the memory effects.

However, one should stress that the model is still highly nonlinear in relation to the deformations and changes of porosity. The second law of

thermodynamics and the objectivity yield then the following constitutive relations for partial stress tensors in isotropic poroelastic materials

$$\begin{aligned}
 \mathbf{P}^S &= \rho^S \frac{\partial \psi^S}{\partial \mathbf{F}^S} + \beta(n - n_E) J^S \mathbf{F}^{S-T} - \\
 &\quad - z^F \rho_{12} \mathbf{F}^S \mathbf{X}'^F \otimes \mathbf{X}'^F, \\
 \mathbf{P}^F &= \rho_t^{F2} \frac{\partial \psi^F}{\partial \rho_t^F} - \beta(n - n_E) J^S \mathbf{F}^{S-T} - \\
 &\quad - (1 - z^F) \rho_{12} \mathbf{F}^S \mathbf{X}'^F \otimes \mathbf{X}'^F,
 \end{aligned} \tag{30}$$

where ψ^S, ψ^F are Helmholtz partial free energy functions depending on the deformations of components, porosity and temperature, $J^S = \det \mathbf{F}^S$ and n_E is the equilibrium porosity dependent on the same arguments as free energy functions. β, z^F are material constants. It is clear that Bowen's model does not contain an influence of the nonequilibrium changes of porosity as well as a quadratic dependence on the relative velocity which follows from the influence of relative acceleration. The deviation of the Bowen model is even more obvious when we include farther nonlinear effects such as a nonlinear diffusion coefficient.

1.6. Concluding remarks

The structure of a thermodynamic model presented in this note indicates three features of nonlinear modelling of porous materials which were not following from the pioneering works of R. M. Bowen. The first one is a different form and structure of Lagrangian balance laws. This follows from the fact that Bowen was using distinct reference configurations for each component which is both physically and mathematically incorrect. The second one is a complex constitutive dependence on diffusion velocities which does not follow in the case of simplified structure of fluxes in Bowen's model which is in turn the consequence of the erroneous Lagrangian formulation of Bowen's model. The third one is the reference to the relative accelerations and, consequently, to the added mass contributions as agents following from tortuosity. According to the second law of thermodynamics this cannot be the case as the first one is nondissipative while the second one must yield a dissipation.

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