

Continuum Theories of Mixtures – Lecture Notes

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1 Introduction

Continuum theories of multicomponent systems can be roughly divided into three groups:

- systems without diffusion (i.e. relative motion of components); the most prominent examples are composites and polycrystals,
- miscible mixtures in which the modelling does not require additional microstructural variables; in special cases (e.g. quasistatic processes) diffusion processes are described in such systems by Fick’s laws,
- immiscible mixtures which do require additional microstructural variables (porosity, degree of saturation, etc.); in special cases diffusion processes are described in such systems by Darcy’s laws.

This classification is not sharp as, for example, in many polycrystals diffusion processes may play an important role (e.g. by solid-solid phase transformations), suspensions may behave almost as granular materials (immiscible mixtures) and require microstructural variables such as the size distribution of grains or they may behave as mixtures of fluids (miscible mixtures).

Modern continuum models of mixtures of fluids have been initiated in 1957 by a series of articles of C. Truesdell (e.g. see: [45]) who presented a systematic construction of a continuous approach to multicomponent fluid systems. He was able to incorporate numerous *ad hoc* models of fluid mixtures developed by A. Fick (1855), J. Stefan (1871), G. Jaumann (1911) and many others. The purely mechanical model developed by Truesdell and some others was essentially extended and corrected by I. Müller (1968) and gave rise to the modern thermodynamical theory of miscible mixtures. It is presented in some details in the book of I. Müller [34].

We present two groups of models: miscible and immiscible mixtures. In the first case we consider the classical model proposed by C. Truesdell and extended by I. Müller. In the second case we present a model with the balance equation for porosity and its particular cases for small deformations of the skeleton (Biot’s model and the simple mixture model).

It is difficult, if not impossible, to give the full list of references for continuum theories of mixtures. Further we quote only some representative papers and, simultaneously, refer to easily available books and monographs which contain more detailed hints on literature. In particular, the following books are recommended:

S. L. SOO; *Fluid Dynamics of Multiphase Systems*, Blaisdell, Waltham, 1967 (particularly classical modeling of suspensions),

A. C. ERINGEN (ed.); *Continuum Physics*, vol. III: *Mixtures and EM Field Theories*, Academic Press, New York, 1976 (in particular Part I: R. M. Bowen, *Theory of mixtures*)

C. TRUESDELL; *Rational Thermodynamics*, Second Edition, Springer, New York, 1984 (Lectures 5 and 6 with contributions on both miscible and immiscible mixtures),

J. BEAR; *Dynamics of Fluids in Porous Media*, Dover, New York, 1988.

I. MÜLLER; *Thermodynamics*, Pitman, Boston, 1985 (Chapter 6 on miscible mixtures).

K. R. RAJAGOPAL, L. TAO; *Mechanics of Mixtures*, World Scientific, Singapore, 1995.

K. WILMANSKI; *Thermomechanics of Continua*, Springer, Berlin, 1998 (Chapter 10 on immiscible mixtures).

K. HUTTER, K. JÖHNK; *Continuum Methods of Physical Modeling*, Springer, Berlin, 2004 (Chapter 7 on theory of mixtures).

Whenever possible we use in these notes an absolute notation for tensors. If needed representations in Cartesian coordinates are applied. We denote vectors by small boldface letters and tensors of the second order by the capital bold face letters, e.g.

$$\begin{aligned}\mathbf{v} &= v_k \mathbf{e}_k, & \mathbf{T} &= t_{kl} \mathbf{e}_k \otimes \mathbf{e}_l, \\ \mathbf{v} \cdot \mathbf{w} &= \mathbf{v}_k w_k, & \mathbf{T} \mathbf{v} &= t_{kl} v_l \mathbf{e}_k, & \mathbf{T} \cdot \mathbf{S} &= \text{tr } \mathbf{T}^T \mathbf{S} = t_{kl} s_{kl}, \\ \text{grad } \mathbf{v} &= \frac{\partial v_k}{\partial x_l} \mathbf{e}_k \otimes \mathbf{e}_l, & \text{div } \mathbf{v} &= \frac{\partial v_k}{\partial x_k}, & \text{grad } \mathbf{T} &= \frac{\partial t_{kl}}{\partial x_m} \mathbf{e}_k \otimes \mathbf{e}_l \otimes \mathbf{e}_m, \quad \text{etc.}\end{aligned}$$

In the second part of the notes we distinguish between Lagrangian and Eulerian reference systems. Their unit base vectors are denoted: Lagrangian base vectors $\mathbf{G}_K, K = 1, 2, 3$, and Eulerian base vectors $\mathbf{e}_k, k = 1, 2, 3$.

2 Fundamentals of the theory of miscible mixtures

As indicated above the main purpose of the theory of miscible mixtures is to describe the macroscopic behavior of mixtures of fluids (in particular – gases). Such effects as heat conduction, diffusion, chemical reactions, osmosis, etc. should be included. We present also separately an application of the theory of mixtures to multicomponent systems containing charged particles which yields various forms of magnetohydrodynamics. While viscous effects are often important in mixtures, they are left out of consideration here. They may be included but yield technical problems of some extent.

2.1 Thermodynamic processes

It is convenient to describe mixtures of fluids, as we do in the fluid dynamics, in the Eulerian reference. It means the current configuration is the reference configuration for the motion. All fields of the model are functions of the spacial variable $\mathbf{x} \in \mathcal{B}_t$ and the time variable $t \in \mathcal{T}$. The domain of the mixture \mathcal{B}_t depends on time and in any instant of time each point of this domain is occupied simultaneously by particles of all components of the mixture. We distinguish the components by the index α running from 1 to A , where A is the number of components.

In the case of thermomechanical systems considered in this Chapter the *thermodynamic process* in the above system is assumed to be described by the following fields

$$\{\rho^\alpha, \mathbf{v}^\alpha, T\}, \quad \alpha = 1, \dots, A, \quad (1)$$

where ρ^α are the current partial mass densities of components referring to the common unit volume in the current configuration \mathcal{B}_t , \mathbf{v}^α are the velocity fields of components and T denotes the absolute temperature common for all components. The last quantity requires an assumption that all components possess the same temperature. In many practical applications this assumption is not satisfied and we demonstrate an example further in these notes. However, the problem of thermodynamic modeling of multicomponent systems with multiple temperatures is still not fully solved and, as we see further, we are able to produce only partial results.

Field equations for the fields (1) follow from the partial balance equations of mass and momentum and from the energy balance equation for the mixture. The partial balance equations for $\alpha = 1, \dots, A$ have the form

$$\frac{d}{dt} \int_{\mathcal{P}_t^\alpha} \rho^\alpha dV = \int_{\mathcal{P}_t^\alpha} \hat{\rho}^\alpha dV, \quad (2)$$

$$\frac{d}{dt} \int_{\mathcal{P}_t^\alpha} \rho^\alpha \mathbf{v}^\alpha dV = \oint_{\partial \mathcal{P}_t^\alpha} \mathbf{T}^\alpha \mathbf{n} dS + \int_{\mathcal{P}_t^\alpha} (\rho^\alpha \mathbf{b}^\alpha + \hat{\mathbf{p}}^\alpha) dV, \quad (3)$$

$$\begin{aligned} \frac{d}{dt} \int_{\mathcal{P}_t^\alpha} \rho^\alpha \left(\varepsilon^\alpha + \frac{1}{2} \mathbf{v}^\alpha \cdot \mathbf{v}^\alpha \right) dV &= \oint_{\partial \mathcal{P}_t^\alpha} (\mathbf{T}^\alpha \mathbf{v}^\alpha - \mathbf{q}^\alpha) \cdot \mathbf{n} dS + \\ &+ \int_{\mathcal{P}_t^\alpha} (\rho^\alpha \mathbf{b}^\alpha \cdot \mathbf{v}^\alpha + \rho^\alpha r^\alpha + \hat{\varepsilon}^\alpha) dV, \end{aligned} \quad (4)$$

where $\mathcal{P}_t^\alpha \subset \mathcal{B}_t$ is a measurable subset of the current configuration which moves with the kinematics of the α -component and $\partial\mathcal{P}_t^\alpha$ denotes its surface with the unit outward normal vector \mathbf{n} . The quantities with the hat are volume densities of sources and, according to the fundamental assumption of Truesdell's mixture theory they must satisfy the following conservation laws

$$\sum_{\alpha=1}^A \hat{\rho}^\alpha = 0, \quad \sum_{\alpha=1}^A \hat{\mathbf{p}}^\alpha = 0, \quad \sum_{\alpha=1}^A \hat{\varepsilon}^\alpha = 0. \quad (5)$$

The remaining quantities $\mathbf{T}^\alpha, \mathbf{b}^\alpha, \varepsilon^\alpha, \mathbf{q}^\alpha, r^\alpha$ denote the symmetric partial Cauchy stress tensor in the α -component, the body force per unit mass of the α -component, the partial density of the internal energy of the α -component, the partial heat flux in the α -component, and the density of energy radiation in the α -component, respectively.

In the case of the single temperature field the partial energy balance equations are not used and we need only the energy conservation of the mixture. This must have, of course, the classical form

$$\frac{d}{dt} \int_{\mathcal{P}_t} \rho \left(\varepsilon + \frac{1}{2} \mathbf{v} \cdot \mathbf{v} \right) dV = \oint_{\partial\mathcal{P}_t} (\mathbf{T}\mathbf{v} - \mathbf{q}) \cdot \mathbf{n} dS + \int_{\mathcal{P}_t} \rho (\mathbf{b} \cdot \mathbf{v} + r) dV. \quad (6)$$

We obtain indeed this relation if we add equations (4) and introduce the definitions

$$\begin{aligned} \rho &= \sum_{\alpha=1}^A \rho^\alpha, \quad \rho \mathbf{v} = \sum_{\alpha=1}^A \rho^\alpha \mathbf{v}^\alpha, \quad \rho \varepsilon = \sum_{\alpha=1}^A \rho^\alpha \left(\varepsilon^\alpha + \frac{1}{2} \mathbf{u}^\alpha \cdot \mathbf{u}^\alpha \right), \\ \mathbf{T} &= \sum_{\alpha=1}^A (\mathbf{T}^\alpha - \rho^\alpha \mathbf{u}^\alpha \otimes \mathbf{u}^\alpha), \quad \mathbf{q} = \sum_{\alpha=1}^A (\mathbf{q}^\alpha + \rho^\alpha (\varepsilon^\alpha + \frac{1}{2} \mathbf{u}^\alpha \cdot \mathbf{u}^\alpha) \mathbf{u}^\alpha - \mathbf{T}^\alpha \mathbf{u}^\alpha), \\ \rho r &= \sum_{\alpha=1}^A \rho^\alpha (r^\alpha + \mathbf{b}^\alpha \cdot \mathbf{u}^\alpha), \quad \mathbf{u}^\alpha = \mathbf{v}^\alpha - \mathbf{v}, \quad \sum_{\alpha=1}^A \rho^\alpha \mathbf{u}^\alpha = 0. \end{aligned} \quad (7)$$

The presence of convective terms containing the *diffusion velocities* \mathbf{u}^α follows from the fact that subsets \mathcal{P}_t of the current configuration \mathcal{B}_t possess the kinematics of the *barycentric velocity field* \mathbf{v} and it means that fluxes contain additional contributions – none of these subsets is *material* with respect to any of the components.

It can be easily checked that the above definitions yield as well the classical conservation of mass and momentum for the whole mixture

$$\frac{d}{dt} \int_{\mathcal{P}_t} \rho dV = 0, \quad \frac{d}{dt} \int_{\mathcal{P}_t} \rho \mathbf{v} dV = \oint_{\partial\mathcal{P}_t} \mathbf{T} \mathbf{n} dS + \int_{\mathcal{P}_t} \rho \mathbf{b} dV, \quad \rho \mathbf{b} = \sum_{\alpha=1}^A \rho^\alpha \mathbf{b}^\alpha. \quad (8)$$

Let us remark that the presence of diffusion yields a macroscopic heat flux \mathbf{q} even in the case when the partial heat conduction contributions \mathbf{q}^α are absent. This property is essential for a peculiar form of the second law of thermodynamics of mixtures which we discuss further.

The above global balance equations yield in a standard way local laws. They have different form in *regular* points in which fields are continuous and in *singular* points on surfaces on which fields may suffer jumps. Namely

$$\begin{aligned}\frac{\partial \rho^\alpha}{\partial t} + \operatorname{div}(\rho^\alpha \mathbf{v}^\alpha) &= \hat{\rho}^\alpha, \\ \frac{\partial \rho^\alpha \mathbf{v}^\alpha}{\partial t} + \operatorname{div}(\rho^\alpha \mathbf{v}^\alpha \otimes \mathbf{v}^\alpha - \mathbf{T}^\alpha) &= \rho^\alpha \mathbf{b}^\alpha + \hat{\mathbf{p}}^\alpha, \\ \frac{\partial \rho \varepsilon}{\partial t} + \operatorname{div}(\rho \varepsilon \mathbf{v} + \mathbf{q}) &= \mathbf{T} \cdot \operatorname{grad} \mathbf{v} + \rho r,\end{aligned}\tag{9}$$

in regular points. The last equation, the so called balance of internal energy, follows by elimination of the contribution of kinetic energy by means of mass and momentum conservation laws.

In singular points the balance equations have the form of jump conditions across the surface. We use them here only for bulk mass of the mixture and the bulk energy of the mixture but, of course, they may be easily derived for all other equations as well. We have for these two quantities

$$\begin{aligned}[[\rho(\mathbf{v} \cdot \mathbf{n} - c)]] &= 0, \quad [[\dots]] = (\dots)^+ - (\dots)^-, \\ [[\mathbf{q} \cdot \mathbf{n}]] &= [[\mathbf{T}(\mathbf{v} - c\mathbf{n})]] \cdot \mathbf{n} - \left[\left[\varepsilon + \frac{1}{2}(\mathbf{v} - c\mathbf{n}) \cdot (\mathbf{v} - c\mathbf{n})\right]\right] \rho(\mathbf{v} \cdot \mathbf{n} - c),\end{aligned}\tag{10}$$

where c denotes the speed of the surface and \mathbf{n} is the unit normal vector to this surface. As indicated the double parenthesis denotes the difference of limits on both sides of the singular surface.

2.2 General constitutive relations for fluid mixtures

Let us begin with the specification of mass sources for chemical reactions. Components of the mixture are then not the most fundamental ingredients of the macroscopic picture. These are rather molecules (constituents) which satisfy laws of mass conservation. To see this structure let us consider the simplest example of formation of water from hydrogen H and oxygen O . These two are molecules (constituents) while the mixture consists of the following components: H, O, H_2, O_2, OH, H_2O . They are participating in chemical reactions which can be symbolically written in the form

$$\begin{aligned}H_2 - 2H &= 0, \\ O_2 - 2O &= 0, \\ H + O - OH &= 0, \\ H + OH - H_2O &= 0, \\ 2H_2 + O_2 - 2H_2O &= 0.\end{aligned}\tag{11}$$

The matrix of coefficients $\gamma_\alpha^r, \alpha = 1, \dots, 6, r = 1, \dots, 5$ in this set of relations is called the *stoichiometric matrix*. Its rank determines the number of independent reactions. In our

example this rank is equal to 4. The conservation of mass for molecules (constituents) in each reaction can be written in the form

$$\sum_{\alpha=1}^A \gamma_{\alpha}^r M_{\alpha} \mu_H = 0, \quad r = 1, \dots, \mathcal{R}, \quad (12)$$

where M_{α} denotes the molecular weight of the component α , μ_H is the mass of a hydrogen atom and \mathcal{R} is the number of reactions.

Further we consider only the set of independent chemical reactions and we denote their number by ν . The contribution of each reaction to the production of components depends also on the *rate of reaction* which we denote by $\lambda^r, r = 1, \dots, \nu$. Then the mass source in partial mass balance equations can be written in the form

$$\hat{\rho}^{\alpha} = \sum_{r=1}^{\nu} \gamma_{\alpha}^r M_{\alpha} \mu_H \lambda^r. \quad (13)$$

It is clear that the conservation relations (12) imply (5)₁.

We proceed to transform the balance equations (9) into field equations for the fields (1). We use the strategy of continuum thermodynamics and assume that the *constitutive quantities*

$$\mathcal{F} = \{\lambda^r, \mathbf{T}^{\alpha}, \hat{\mathbf{p}}^{\alpha}, \varepsilon, \mathbf{q}\}, \quad (14)$$

are sufficiently smooth functions of *constitutive variables*. The choice of the constitutive variables specifies the class of substances admissible in the model under construction. We follow here the case considered by I. Müller [34] and consider inviscid fluids. We include among constitutive variables the gradients of partial mass densities. It has been shown by I. Müller that this yields a desirable structure of interactions of components. We return later to this point. The chosen set of constitutive variables is as follows

$$\mathcal{C} = \{\rho^{\alpha}, \text{grad } \rho^{\alpha}, \mathbf{v}^{\alpha}, T, \text{grad } T\}. \quad (15)$$

Hence the *closure* of the set of balance equations has the form

$$\mathcal{F} = \mathcal{F}(\mathcal{C}). \quad (16)$$

These relations must satisfy the conservation restrictions (5)₂.

In order to describe viscous fluids we would have to add a dependence on gradients of velocity to the set of constitutive variables. This can be easily done but the results are not so transparent as in the present case.

2.3 Material objectivity

The principle of material objectivity (material frame indifference) concerns the behavior of field equations under the so-called Euclidean transformation. This transformation follows from the assumption that the configuration space is *isometric*. This means that two arbitrary points of the material system at the instant of time t , say \mathbf{x}_1 and \mathbf{x}_2 , transform in the new frame into \mathbf{x}_1^* and \mathbf{x}_2^* , respectively, preserving the distance, i.e. the following condition is satisfied

$$|\mathbf{x}_1 - \mathbf{x}_2| = |\mathbf{x}_1^* - \mathbf{x}_2^*|.$$

This is indeed the case if the transformation is described by the following relation for an arbitrary point of the configuration space

$$\mathbf{x}^* = \mathbf{O}(t) \mathbf{x} + \mathbf{c}(t), \quad \mathbf{O}^T = \mathbf{O}^{-1}. \quad (17)$$

Clearly, the orthogonal tensor \mathbf{O} describes the rotation of the frame and the vector \mathbf{c} the translation, both dependent on time in an arbitrary manner. We assume that this dependence is sufficiently smooth.

Scalar a , vector \mathbf{w} , and tensor \mathbf{T} transform in an objective manner if they satisfy the following transformation rules

$$a^* = a, \quad \mathbf{w}^* = \mathbf{O}\mathbf{w}, \quad \mathbf{T}^* = \mathbf{O}\mathbf{T}\mathbf{O}^T. \quad (18)$$

Obviously, neither the velocity nor the acceleration transform in an objective manner. Differentiation of (17) with respect to time yields

$$\begin{aligned} \mathbf{v}^* &= \mathbf{O}\mathbf{v} + \dot{\mathbf{O}}\mathbf{x} + \dot{\mathbf{c}}, \quad \dot{\mathbf{O}} = \frac{d\mathbf{O}}{dt}, \quad \dot{\mathbf{c}} = \frac{d\mathbf{c}}{dt} \\ \mathbf{a}^* &= \frac{\partial \mathbf{v}}{\partial t} + \mathbf{v}^* \cdot \text{grad } \mathbf{v}^* = \mathbf{O}\mathbf{a} + 2\dot{\mathbf{O}}\mathbf{v} + \ddot{\mathbf{O}}\mathbf{x} + \ddot{\mathbf{c}}. \end{aligned} \quad (19)$$

Consequently, the momentum balance equations do not transform in an objective manner. The transformation from an inertial to a noninertial frame yields centrifugal, Coriolis, Euler, and translational forces known from the classical mechanics. Simultaneously, the mass and energy balance equations transform in an objective manner (e.g. comp. [32]).

In the case of chemical reactions there appears an additional problem related to the contribution of mass sources to the momentum balance equations. It becomes clear when we use the chain rule of differentiation on the left hand side of (9)₂ and substitute mass balance equations (9)₁. Then the above described structure remains unchanged if we assume that the following vector

$$\hat{\mathbf{p}}^\alpha - \hat{\rho}^\alpha \mathbf{v}^\alpha, \quad (20)$$

is objective rather than the momentum source itself. We do so in further considerations.

The principle of material objectivity (material frame indifference) requires that functions

$$\mathcal{F}_o = \{\lambda^r, \mathbf{T}^\alpha, \hat{\mathbf{p}}^\alpha - \hat{\rho}^\alpha \mathbf{v}^\alpha, \varepsilon, \mathbf{q}\} = \mathcal{F}_o(\mathcal{C}), \quad (21)$$

remain unchanged under an arbitrary Euclidean transformation, i.e.

$$\mathcal{F}_o^* = \mathcal{F}_o(\mathcal{C}^*). \quad (22)$$

Note that the constitutive *function* $\mathcal{F}_o(\cdot)$ is the same in (21) and (22).

An immediate consequence of the above principle is the elimination of one of velocities among constitutive variables. Instead of partial velocities this set may contain only relative velocities which are objective. These may be diffusion velocities \mathbf{u}^α , or, as they are only $A - 1$ independent variables of this art, relative velocities

$$\mathbf{w}^\alpha = \mathbf{v}^\alpha - \mathbf{v}^A, \quad (23)$$

which are more convenient in the calculations.

The full representation of constitutive functions in their objective form is a rather complicated task and we shall not do so in these notes. We limit our attention to constitutive functions which are linear in $\text{grad } \rho^\alpha$, \mathbf{w}^α , $\text{grad } T$. In this case the most general form of the constitutive equations compatible with the material objectivity is as follows

$$\begin{aligned}
\lambda^r &= \lambda^r(\rho^\beta, T), \\
\mathbf{T}^\alpha &= -p^\alpha(\rho^\beta, T) \mathbf{1}, \\
\hat{\mathbf{p}}^\alpha - \hat{\rho}^\alpha \mathbf{v}^\alpha &= \sum_{\beta=1}^A M_\rho^{\alpha\beta} \text{grad } \rho^\beta + \sum_{\beta=1}^{A-1} M_w^{\alpha\beta} \mathbf{w}^\beta + M_T^\alpha \text{grad } T, \\
\mathbf{q}_I &= \sum_{\beta=1}^A q_\rho^\beta \text{grad } \rho^\beta + \sum_{\beta=1}^{A-1} q_w^\beta \mathbf{w}^\beta + q_T \text{grad } T, \\
\varepsilon_I &= \varepsilon_I(\rho^\beta, T),
\end{aligned} \tag{24}$$

where the index I denotes the so-called *intrinsic* part of the quantity

$$\begin{aligned}
\mathbf{q}_I &= \mathbf{q} - \sum_{\alpha=1}^A \frac{1}{2} \rho^\alpha (\mathbf{u}^\alpha \cdot \mathbf{u}^\alpha) \mathbf{u}^\alpha = \sum_{\alpha=1}^A \mathbf{q}^\alpha + \sum_{\alpha=1}^A (\rho^\alpha \varepsilon^\alpha \mathbf{1} - \mathbf{T}^\alpha) \mathbf{u}^\alpha, \\
\varepsilon_I &= \varepsilon - \sum_{\alpha=1}^A \frac{1}{2} \frac{\rho^\alpha}{\rho} \mathbf{u}^\alpha \cdot \mathbf{u}^\alpha = \sum_{\alpha=1}^A \frac{\rho^\alpha}{\rho} \varepsilon^\alpha.
\end{aligned} \tag{25}$$

The coefficients appearing in relations (24) may be dependent on ρ^β and T . However, they are not independent due to the previously discussed restrictions on sources. Namely we have

$$\begin{aligned}
\sum_{\alpha=1}^A M_\rho^{\alpha\beta} &= 0, \quad \beta = 1, \dots, A, \\
\sum_{\alpha=1}^A M_w^{\alpha\beta} + \hat{\rho}^\beta &= 0, \quad \beta = 1, \dots, A-1, \\
\sum_{\alpha=1}^A M_T^\alpha &= 0.
\end{aligned} \tag{26}$$

In spite of the above assumed linearity the whole model remains nonlinear due to various nonlinear explicit contributions.

2.4 Second law of thermodynamics

2.4.1 Evaluation of the entropy inequality

The strategy of continuum thermodynamics in construction of macroscopic models relies on the assumption that solutions of the field equations identically satisfy the second law of thermodynamics called also the entropy principle. This law consists of four parts:

i/ There exist a nontrivial entropy density function η and the entropy flux \mathbf{h} which are both constitutive. In the case of miscible mixtures, considered in this Section, they must have the following general form

$$\eta = \eta(\rho^\beta, T), \quad \mathbf{h} = \sum_{\alpha=1}^A h_\rho^\alpha \text{grad } \rho^\alpha + \sum_{\alpha=1}^{A-1} h_w^\alpha \mathbf{w}^\alpha + h_T \text{grad } T, \quad (27)$$

where $h_\rho^\alpha, h_w^\alpha$, and h_T may be functions of ρ^β, T .

ii/ The entropy density satisfies the balance equation whose form in regular points is as follows

$$\frac{\partial \rho \eta}{\partial t} + \text{div}(\rho \eta \mathbf{v} + \mathbf{h}) = \sigma, \quad (28)$$

where σ denotes the entropy source.

iii/ The entropy source is nonnegative for all solutions of field equations, i.e. for all thermodynamic processes. Consequently, the following inequality holds

$$\forall_{\text{all thermodynamic processes}} \frac{\partial \rho \eta}{\partial t} + \text{div}(\rho \eta \mathbf{v} + \mathbf{h}) \geq 0. \quad (29)$$

iv/ There exist *ideal walls* on which there is no entropy production and the temperature is continuous across it, i.e.

$$[[\mathbf{h} \cdot \mathbf{n}]] + [[\eta]] \rho(\mathbf{v} \cdot \mathbf{n} - c) = 0, \quad [[T]] = 0. \quad (30)$$

I-Shih Liu (e.g. [32], [34]) has proposed a method of exploitation of the inequality (29) which reminds the classical method of Lagrange multipliers in mechanics. Namely, instead of this inequality restricting the solutions of field equations we consider solutions of an extended inequality which should hold for *all fields*. This can be done if we consider field equations as constraints on solutions of the entropy inequality. Such constraints can be eliminated by multipliers and the extended form of the inequality is as follows

$$\begin{aligned} & \forall_{\text{all fields}} \frac{\partial \rho \eta}{\partial t} + \text{div}(\rho \eta \mathbf{v} + \mathbf{h}) - \sum_{\alpha=1}^A \Lambda^{\rho^\alpha} \left(\frac{\partial \rho^\alpha}{\partial t} + \text{div}(\rho^\alpha \mathbf{v}^\alpha) - \sum_{r=1}^{\nu} \gamma_\alpha^r M_{\alpha\mu_H} \lambda^r \right) - \\ & - \sum_{\alpha=1}^A \Lambda^{v^\alpha} \cdot \left(\frac{\partial \rho^\alpha \mathbf{v}^\alpha}{\partial t} + \text{div}(\rho^\alpha \mathbf{v}^\alpha \otimes \mathbf{v}^\alpha - \mathbf{T}^\alpha) - \hat{\mathbf{p}}^\alpha \right) - \\ & - \Lambda^\varepsilon \left(\frac{\partial \rho \varepsilon}{\partial t} + \text{div}(\rho \varepsilon \mathbf{v} + \mathbf{q}) - \mathbf{T} \cdot \text{grad } \mathbf{v} \right) \geq 0. \end{aligned} \quad (31)$$

The Lagrange multipliers $\Lambda^{\rho^\alpha}, \Lambda^{v^\alpha}, \Lambda^\varepsilon$ are functions of constitutive variables $\rho^\beta, \text{grad } \rho^\beta, \mathbf{v}^\beta, T, \text{grad } T$. After the exploitation of the above inequality these multipliers must be eliminated as auxiliary quantities.

Insertion of constitutive relations into the inequality (31) leads to an inequality which is explicitly linear in the derivatives

$$\left\{ \frac{\partial T}{\partial t}, \text{grad} \otimes \text{grad } T, \frac{\partial \rho^\beta}{\partial t}, \text{grad} \otimes \text{grad } \rho^\beta, \frac{\partial \mathbf{v}^\beta}{\partial t}, \text{grad } \mathbf{v}^\beta \right\}. \quad (32)$$

Since the inequality (31) must hold for arbitrary fields these derivatives can be chosen arbitrarily. Consequently, the inequality can be violated if these contributions do not vanish identically. This yields a series of identities which, on the one hand side, determine multipliers and, on the other hand, restrict constitutive relations. In addition, there remains a nonlinear part of the inequality, the so-called *residual* inequality which determines the *dissipation* density of processes.

We quote only one of the consequences of these identities

$$\Lambda^\varepsilon \sum_{\alpha=1}^A p^\alpha = - \sum_{\alpha=1}^A \rho^\alpha \Lambda_I^{\rho^\alpha} + \rho (\eta - \Lambda^\varepsilon \varepsilon_I), \quad (33)$$

where

$$\Lambda_I^{\rho^\beta} = \Lambda^{\rho^\beta} - \frac{1}{T} (\mathbf{v}^\beta \cdot \mathbf{u}^\beta - \frac{1}{2} \mathbf{u}^\beta \cdot \mathbf{u}^\beta) = \Lambda_I^{\rho^\beta}(\rho^\alpha, T). \quad (34)$$

For further details we refer the reader to the following Appendix and to the book of Ingo Müller [34].

2.4.2 Appendix: identities following from the entropy inequality

$$\frac{\partial \eta}{\partial T} - \Lambda^\varepsilon \frac{\partial \varepsilon}{\partial T} = 0,$$

$$\frac{\partial \mathbf{h}}{\partial \mathbf{g}} - \Lambda^\varepsilon \frac{\partial \mathbf{q}}{\partial \mathbf{g}} = 0, \quad \mathbf{g} = \text{grad } T,$$

$$\frac{\partial \eta}{\partial \rho^\beta} - \Lambda^\varepsilon \frac{\partial \varepsilon}{\partial \rho^\beta} + \frac{1}{\rho} (\eta - \Lambda^\varepsilon \varepsilon) - \frac{1}{\rho} \Lambda^{\rho^\beta} - \frac{1}{\rho} \mathbf{v}^\beta \cdot \mathbf{\Lambda}^{v^\beta} = 0,$$

$$\frac{\partial \mathbf{h}}{\partial \text{grad } \rho^\beta} - \Lambda^\varepsilon \frac{\partial \mathbf{q}}{\partial \text{grad } \rho^\beta} = 0,$$

$$\frac{\partial \eta}{\partial \mathbf{w}^\beta} - \Lambda^\varepsilon \frac{\partial \varepsilon}{\partial \mathbf{w}^\beta} - \frac{\rho^\beta}{\rho} \mathbf{\Lambda}^{v^\beta} = 0, \quad \beta = 1, \dots, A-1,$$

$$- \sum_{\beta=1}^A \left(\frac{\partial \eta}{\partial \mathbf{w}^\beta} - \Lambda^\varepsilon \frac{\partial \varepsilon}{\partial \mathbf{w}^\beta} \right) - \frac{\rho^A}{\rho} \mathbf{\Lambda}^{v^A} = 0,$$

$$\left(\frac{\partial \eta}{\partial \rho^\alpha} - \Lambda^\varepsilon \frac{\partial \varepsilon}{\partial \rho^\alpha} \right) \mathbf{1} - \frac{1}{\rho \rho^\alpha} \left(\frac{\partial \mathbf{h}}{\partial \mathbf{w}^\alpha} - \Lambda^\varepsilon \frac{\partial \mathbf{q}}{\partial \mathbf{w}^\alpha} \right) + \frac{1}{\rho} \mathbf{\Lambda}^{v^\alpha} \otimes \mathbf{u}^\alpha - \frac{1}{\rho^2} \Lambda^\varepsilon \mathbf{T} = 0, \\ \alpha = 1, \dots, A-1$$

$$\left(\frac{\partial \eta}{\partial \rho^A} - \Lambda^\varepsilon \frac{\partial \varepsilon}{\partial \rho^A} \right) \mathbf{1} - \sum_{\beta=1}^{A-1} \frac{1}{\rho \rho^A} \left(\frac{\partial \mathbf{h}}{\partial \mathbf{w}^\beta} - \Lambda^\varepsilon \frac{\partial \mathbf{q}}{\partial \mathbf{w}^\beta} \right) - \frac{1}{\rho} \mathbf{\Lambda}^{v^A} \otimes \mathbf{u}^A - \frac{1}{\rho^2} \Lambda^\varepsilon \mathbf{T} = 0.$$

Residual inequality

$$\begin{aligned}
& \sum_{\beta=1}^A \left[\left(\frac{\partial \mathbf{h}}{\partial \rho^\beta} - \Lambda^\varepsilon \frac{\partial \mathbf{q}}{\partial \rho^\beta} \right) - \rho \left(\frac{\partial \eta}{\partial \rho^\beta} - \Lambda^\varepsilon \frac{\partial \varepsilon}{\partial \rho^\beta} \right) \mathbf{u}^\beta - \right. \\
& \quad \left. - \sum_{\alpha=1}^A \Lambda^{v^\alpha} \frac{\partial p^\alpha}{\partial \rho^\beta} + \Lambda^\varepsilon \frac{1}{\rho} \mathbf{T} \mathbf{u}^\beta \right] \cdot \text{grad } \rho^\beta + \\
& + \left(\frac{\partial \mathbf{h}}{\partial T} - \Lambda^\varepsilon \frac{\partial \mathbf{q}}{\partial T} - \sum_{\alpha=1}^A \Lambda^{v^\alpha} \frac{\partial p^\alpha}{\partial T} \right) \cdot \mathbf{g} + \sum_{\alpha=1}^A \Lambda^{\rho^\alpha} \hat{\rho}^\alpha + \sum_{\alpha=1}^A \Lambda^{v^\alpha} \cdot \hat{\mathbf{p}}^\alpha \geq 0.
\end{aligned}$$

2.4.3 Results for a single fluid

For a single fluid the results follow from the above considerations by setting $A = 1$. We obtain

$$\begin{aligned}
\Lambda^v &= 0, \\
d\eta &= \Lambda^\varepsilon \left(d\varepsilon - \frac{p}{\rho^2} d\rho \right), \\
\mathbf{h} &= \Lambda^\varepsilon \mathbf{q}, \\
\frac{\partial \Lambda^\varepsilon}{\partial \rho} \mathbf{q} \cdot \text{grad } \rho + \frac{\partial \Lambda^\varepsilon}{\partial T} \mathbf{q} \cdot \text{grad } T &\geq 0.
\end{aligned} \tag{35}$$

We use now the part iv/ of the second law of thermodynamics. Let us consider an impermeable ideal wall which separates two different single fluids I and II. Such a wall moves with the speed $c = \mathbf{v} \cdot \mathbf{n}$. The jump condition (30) yields then

$$[[\mathbf{h}]] \cdot \mathbf{n} = 0 \quad \text{and} \quad [[T]] = 0. \tag{36}$$

Bearing (10) and (35)₃ in mind, we obtain

$$\Lambda_I^\varepsilon(\rho_I, T) = \Lambda_{II}^\varepsilon(\rho_{II}, T). \tag{37}$$

This relation must hold for an arbitrary independent choice of ρ_I and ρ_{II} . Hence it can be satisfied only if it is independent of mass densities at all. We conclude

$$\Lambda_I^\varepsilon(T) = \Lambda_{II}^\varepsilon(T). \tag{38}$$

Consequently, the function $\Lambda^\varepsilon(T)$ is the same for all ideal fluids and, for this reason, we call it *universal*.

In order to determine this function it is sufficient to inspect (35)₂ for the case of ideal gases. Then it is identical with $1/T$. Hence it follows in general

$$\Lambda^\varepsilon = \frac{1}{T}. \tag{39}$$

Relations (35) become

$$d\eta = \frac{1}{T} \left(d\varepsilon - \frac{p}{\rho^2} d\rho \right), \quad \mathbf{h} = \frac{1}{T} \mathbf{q}, \quad \mathbf{q} \cdot \text{grad } T \leq 0. \tag{40}$$

These are the results identical with those of the classical thermodynamics. The first relation is called the Gibbs equation.

2.4.4 Ideal walls in mixture

If we consider an impermeable wall separating a mixture I from a single fluid II and account for the jump conditions we obtain immediately

$$\Lambda_I^\varepsilon(\rho_I^\alpha, T) = \frac{1}{T}. \quad (41)$$

Hence the multiplier Λ^ε remains universal also for mixtures.

One cannot argue in the same way in a general model of mixtures in which each component possesses its own temperature. The multipliers of the partial energy balance equations are not in general universal functions of the absolute temperature. This means as well that temperature cannot be measured on the surface of contact between two different systems because such a surface, even if it is an ideal wall, does not yield the continuity of temperatures. Consequently, we cannot construct thermometers.

Let us now consider a semipermeable wall separating two mixtures I and II. The wall is assumed to be permeable for a single chosen component γ . On such a wall

$$\mathbf{v}^\alpha \cdot \mathbf{n} = c \quad \text{for } \alpha \neq \gamma, \quad \mathbf{v} = c\mathbf{n} + \frac{\rho^\gamma}{\rho} (\mathbf{v}^\gamma - c\mathbf{n}). \quad (42)$$

The jump of internal energy (10)₂ reads

$$[[\mathbf{q}]] \cdot \mathbf{n} - \left[\left[\frac{\mathbf{n} \cdot \mathbf{T} \mathbf{n}}{\rho} - \varepsilon - \frac{1}{2} (\mathbf{v} - c\mathbf{n}) \cdot (\mathbf{v} - c\mathbf{n}) \right] \right] \rho (\mathbf{v} \cdot \mathbf{n} - c) = 0,$$

or, bearing the separation (25) and the relation

$$\mathbf{T} = - \sum_{\alpha=1}^A (p^\alpha \mathbf{1} + \rho^\alpha \mathbf{u}^\alpha \otimes \mathbf{u}^\alpha),$$

in mind, we obtain

$$[[\mathbf{q}_I]] \cdot \mathbf{n} + \left[\left[\frac{1}{\rho} \sum_{\alpha=1}^A p^\alpha + \varepsilon_I + \frac{1}{2} (\mathbf{v} - c\mathbf{n}) \cdot (\mathbf{v} - c\mathbf{n}) \right] \right] \rho (\mathbf{v} \cdot \mathbf{n} - c) = 0. \quad (43)$$

Simultaneously, the jump of the entropy is of the following form

$$[[\mathbf{h}]] \cdot \mathbf{n} + [[\eta]] \rho (\mathbf{v} \cdot \mathbf{n} - c) = 0. \quad (44)$$

These two relations can be now substituted in one of the identities following from the evaluation of the entropy inequality. The result is

$$\left[\left[\varepsilon_I - T\eta + \frac{1}{2} (\mathbf{v} - c\mathbf{n}) \cdot (\mathbf{v} - c\mathbf{n}) + \frac{1}{\rho} \sum_{\alpha=1}^A p^\alpha - T \sum_{\alpha=1}^A \left(\delta^{\gamma\beta} - \frac{\rho^\beta}{\rho} \right) \Lambda_I^{\rho^\beta} \right] \right] = 0. \quad (45)$$

Bearing (33) in mind, this relation can be transformed as follows

$$[[\mu^\gamma]] = 0, \quad (46)$$

where

$$\mu^\gamma = \mu_I^\gamma + \frac{1}{2} (\mathbf{v} - c\mathbf{n}) \cdot (\mathbf{v} - c\mathbf{n}), \quad \mu_I^\gamma = -T \Lambda_I^{\rho^\gamma}, \quad (47)$$

This quantity continuous across ideal semipermeable walls is called the *chemical potential of the component* γ . This can be determined experimentally. Namely according to the relation (33) we have

$$\sum_{\alpha=1}^A \rho^\alpha \mu_I^\alpha = \rho (\varepsilon_I - T\eta) + \sum_{\alpha=1}^A p^\alpha, \quad (48)$$

and, for the single fluid,

$$\mu_I = \varepsilon - T\eta + \frac{p}{\rho}, \quad (49)$$

which is, of course, the free enthalpy, and, hence, a measurable quantity. We can now argue in the same way as we did for the temperature. The contact between the mixture and the fluid identical with the γ -component of the mixture through the semipermeable wall for this component yields the measurement of the chemical potential of this component.

The remaining results of the exploitation of the second law of thermodynamics can now be written in the following compact form

$$\begin{aligned} \Lambda^{v^\alpha} &= -\frac{1}{T} \mathbf{u}^\alpha, \\ d(\rho\eta) &= \frac{1}{T} \left(d(\rho\varepsilon_I) - \sum_{\alpha=1}^A \mu_I^\alpha d\rho^\alpha \right), \\ \rho(\varepsilon_I - T\eta) &= \sum_{\alpha=1}^A \rho^\alpha \mu_I^\alpha - p, \\ \mathbf{h} &= \frac{1}{T} \left(\mathbf{q} - \sum_{\alpha=1}^A \rho^\alpha \mu_I^\alpha \mathbf{u}^\alpha \right). \end{aligned} \quad (50)$$

Equation (50)₂ is the Gibbs equation for the mixtures. We investigate further its consequences. Equation (50)₃ is called the Gibbs-Duhem equation. Finally, the relation (50)₄ between the entropy flux \mathbf{h} and the heat flux \mathbf{q} demonstrates the fundamental difference between the thermodynamics of single component media for which $\mathbf{h} = \mathbf{q}/T$ and the multicomponent media. The presence of the additional term in the above relation proves that we cannot rely in thermodynamics of mixtures on the classical Clausius-Duhem inequality as the form of the second law of thermodynamics. This is one of the main observations made by Ingo Müller in the construction of thermodynamic mixture theories.

2.5 Interactions in thermomechanical mixtures, simple mixtures

The above presented Gibbs equation yields immediately the following relations

$$\mu_I^\alpha = \frac{\partial \rho(\varepsilon_I - T\eta)}{\partial \rho^\alpha}, \quad \rho\eta = \frac{\partial \rho(\varepsilon_I - T\eta)}{\partial T}, \quad (51)$$

as well as the integrability conditions

$$\frac{\partial \rho\varepsilon_I}{\partial \rho^\alpha} = -T^2 \frac{\partial (\mu_I^\alpha/T)}{\partial T}, \quad \frac{\partial \mu_I^\alpha}{\partial \rho^\beta} = \frac{\partial \mu_I^\beta}{\partial \rho^\alpha}. \quad (52)$$

Hence the derivatives of the Helmholtz free energy density $\rho(\varepsilon_I - T\eta)$ specify constitutive relations for chemical potentials and for the entropy. In addition, integrability relations demonstrate couplings between components: the chemical potential of component α depends on all other mass densities.

There are some additional restrictions due to the fact that the multiplier Λ^ε is dependent only on the temperature. For this reason the residual inequality contains a contribution linear in $\text{grad } \rho^\alpha$ which must vanish according to the same argument which we made before. This yields the following identity

$$\sum_{\alpha=1}^A \frac{\partial \Lambda_I^{\rho^\alpha}}{\partial \rho^\gamma} \rho^\alpha \mathbf{u}^\alpha + \frac{\partial \Lambda^\varepsilon}{\partial T} q_\rho^\gamma \text{grad } T - \Lambda^\varepsilon \sum_{\alpha=1}^A \left(M_\rho^{\alpha\gamma} - \frac{\partial p^\alpha}{\partial \rho^\gamma} \right) \mathbf{u}^\alpha = 0. \quad (53)$$

Consequently, we obtain

$$q_\rho^\gamma = 0, \quad M_\rho^{\alpha\gamma} = \frac{\partial p^\alpha}{\partial \rho^\gamma} - \rho^\alpha \frac{\partial \mu_I^\alpha}{\partial \rho^\gamma}. \quad (54)$$

This yields the following form of the energy flux and the sources in momentum equations

$$\begin{aligned} \mathbf{q}_I &= q_T \text{grad } T + \sum_{\beta=1}^{A-1} q_w^\beta \mathbf{w}^\beta, \\ \mathbf{m}^\alpha - \hat{\rho}^\alpha \mathbf{v}^\alpha &= M_T^\alpha \text{grad } T + \sum_{\beta=1}^{A-1} M_w^{\alpha\beta} \mathbf{w}^\beta + \sum_{\beta=1}^A \left(\frac{\partial p^\alpha}{\partial \rho^\beta} - \rho^\alpha \frac{\partial \mu_I^\alpha}{\partial \rho^\beta} \right) \text{grad } \rho^\beta. \end{aligned} \quad (55)$$

We see that the only place where the gradient of partial mass densities appears in the model is the source of momentum. However even this weak form of the influence has an important bearing on interactions in the mixture. Namely, if we assume that the gradient of mass densities does not appear at all in the model we obtain from (55)

$$\frac{1}{\rho^\alpha} \frac{\partial p^\alpha}{\partial \rho^\beta} = \frac{\partial \mu_I^\alpha}{\partial \rho^\beta}. \quad (56)$$

This relation yields the following integrability condition

$$-\frac{1}{\rho^{\alpha 2}} \delta^{\alpha\gamma} \frac{\partial p^\alpha}{\partial \rho^\beta} = -\frac{1}{\rho^{\alpha 2}} \delta^{\alpha\beta} \frac{\partial p^\alpha}{\partial \rho^\gamma}.$$

Hence it follows

$$\frac{\partial p^\alpha}{\partial \rho^\beta} = 0 \quad \text{when} \quad \alpha \neq \beta. \quad (57)$$

This means that the partial pressure p^α depends in this case on its mass density ρ^α but not on the mass densities of other components. We say then that the mixture is *simple*. Molecules in such mixtures do not feel forces of interactions created in the material due to heterogeneity. This observation made by Ingo Müller in 1968 (e.g [34]) has solved one of the fundamental problems of the classical theory of mixtures of fluids. We see further that a similar problem arises for immiscible mixtures.

Obviously the relation (56) yields for simple mixtures $\mu_I^\alpha = \mu_I^\alpha(\rho^\alpha, T)$. Hence

$$\frac{\partial^2 \rho (\varepsilon_I - T\eta)}{\partial \rho^\alpha \partial \rho^\beta} = 0 \quad \text{for } \alpha \neq \beta. \quad (58)$$

Consequently the free energy is the sum of functions which depend on only one mass density and temperature. The entropy density possesses the same property and so does the internal energy. Therefore we can write

$$\rho \varepsilon_I = \sum_{\alpha=1}^A \rho^\alpha \varepsilon^\alpha(\rho^\alpha, T), \quad \rho \eta = \sum_{\alpha=1}^A \rho^\alpha \eta^\alpha(\rho^\alpha, T). \quad (59)$$

This decomposition shows that there is no energy of interaction between components in simple mixtures. It yields as well the following relation for chemical potentials

$$\mu_I^\alpha = \varepsilon^\alpha - T\eta^\alpha + \frac{p^\alpha}{\rho^\alpha}, \quad (60)$$

which means that in simple mixtures the chemical potential and the partial free enthalpy are identical.

We proceed to investigate the residual inequality which remains after the analysis presented above. It has the form

$$\begin{aligned} \mathcal{D} := & \left(\begin{array}{c} \text{grad } T \\ \mathbf{w}^\alpha \end{array} \right) \cdot \left(\begin{array}{cc} -\frac{q_T}{A^\alpha} & A^\beta \\ A^\alpha & -\frac{1}{T} M_w^{\alpha\beta} \end{array} \right) \left(\begin{array}{c} \text{grad } T \\ \mathbf{w}^\beta \end{array} \right) - \\ & - \frac{1}{T} \sum_{r=1}^{\nu} \left(\sum_{\alpha=1}^{A-1} (\mu_I^\alpha - \mu_I^A + \frac{1}{2} \mathbf{w}^\alpha \cdot \mathbf{w}^\alpha) \gamma_\alpha^r M_\alpha \mu_H \lambda^r \right) \geq 0, \end{aligned} \quad (61)$$

where

$$\begin{aligned} A^\alpha = & -\frac{1}{2T} \left\{ \frac{q_w^\alpha}{T} + \left[\left(\frac{M_T^\alpha}{\rho^\alpha} - \frac{M_T^\gamma}{\rho^\gamma} \right) - \left(\frac{1}{\rho^\alpha} \frac{\partial p^\alpha}{\partial T} - \frac{1}{\rho^\gamma} \frac{\partial p^\gamma}{\partial T} \right) + \right. \right. \\ & \left. \left. + T \frac{\partial \frac{\mu_I^\alpha - \mu_I^\gamma}{T}}{\partial T} \right] \sum_{\gamma=1}^{A-1} \left(\rho^\alpha \delta^{\alpha\gamma} - \frac{\rho^\alpha \rho^\gamma}{\rho} \right) \right\}. \end{aligned} \quad (62)$$

The function \mathcal{D} is called the *dissipation density* and it consists of four contributions:

- chemical reactions which are primarily characterized by the difference of chemical potentials $\mu_I^\alpha - \mu_I^A$,
- heat conduction which contributes with the square of the temperature gradient $\text{grad } T$,
- diffusion which contributes with the square of the relative velocity \mathbf{w}^α ,
- thermal diffusion which contributes with the product of the temperature gradient and relative velocity.

The vanishing dissipation defines the *thermodynamic equilibrium*. As this state corresponds to the minimum of dissipation there are additional conditions – thermodynamic stability conditions of equilibrium. We shall not present them in these notes.

3 Mixture models of charged particles, plasmas (magnetohydrodynamics – MHD)

3.1 Preliminaries

The continuous models of mixtures can be also constructed for systems consisting of charged particles. We present here only a simple version of such a model in which these particles do not possess any structure. With an additional condition of the so-called electric neutrality this model describes gaseous plasma in some ranges of parameters (e.g. [37], [29], [26]). In Fig. 1 we show roughly different forms of plasma for various temperatures and electron densities. It is seen that the mixture model leading to the so-called magnetohydrodynamics (MHD) is appropriate only in a rather limited region of these parameters. Thermodynamics of single component continuum in electromagnetic fields is described in details in the book of I. Müller [34] (see also: [33]).

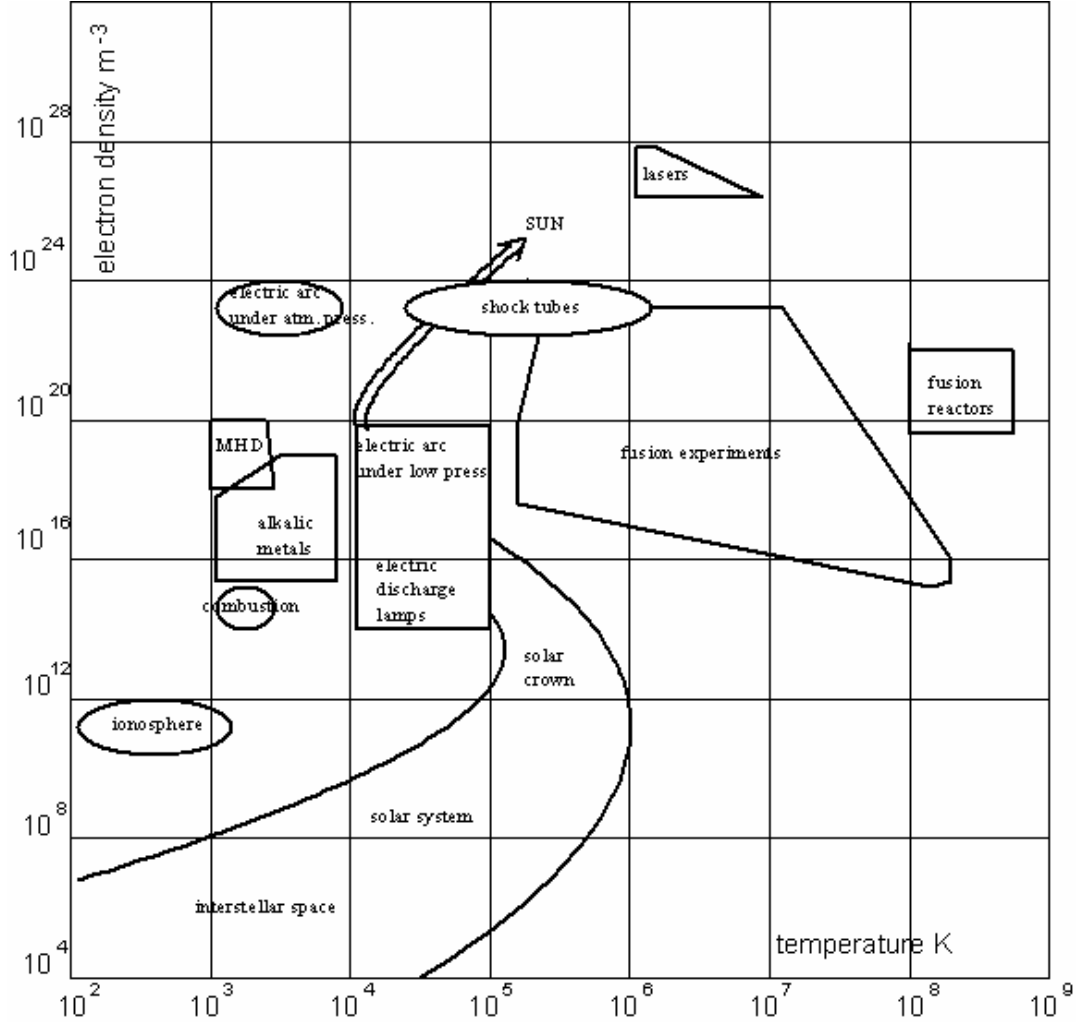


Figure 1: *Different properties of plasma appearing in nature*

3.2 Fundamental equations for mixtures in electromagnetic field

The aim of the continuum mixture theory in electromagnetic field is to determine the following fields

- n^α – particle density of type α whose molecular mass is equal to m^α ,
- \mathbf{v}^α – velocity field of particles of component α ,
- T^α – temperature field of the component α ,
- \mathbf{E} – electric field,
- \mathbf{H} – magnetic field.

All these fields are functions of the point \mathbf{x} and time t .

Field equations are constructed on the basis of balance equations which in the present case have the following global form

$$\frac{d}{dt} \int_{\mathcal{P}_t^\alpha} m^\alpha n^\alpha dV = \int_{\mathcal{P}_t^\alpha} \hat{\rho}^\alpha dV, \quad (63)$$

$$\frac{d}{dt} \int_{\mathcal{P}_t^\alpha} m^\alpha n^\alpha \mathbf{v}^\alpha dV = \oint_{\partial \mathcal{P}_t^\alpha} \mathbf{T}^\alpha \mathbf{n} dS + \int_{\mathcal{P}_t^\alpha} e^\alpha n^\alpha (\mathbf{E} + \mathbf{v}^\alpha \times \mathbf{B}) dV + \quad (64)$$

$$+ \int_{\mathcal{P}_t^\alpha} (\rho^\alpha \mathbf{b}^\alpha + \hat{\mathbf{p}}^\alpha) dV,$$

$$\frac{d}{dt} \int_{\mathcal{P}_t^\alpha} m^\alpha n^\alpha \left(\varepsilon^\alpha + \frac{1}{2} \mathbf{v}^\alpha \cdot \mathbf{v}^\alpha \right) dV = \oint_{\partial \mathcal{P}_t^\alpha} (\mathbf{T}^\alpha \mathbf{v}^\alpha - \mathbf{q}^\alpha) \cdot \mathbf{n} dS +$$

$$+ \int_{\mathcal{P}_t^\alpha} e^\alpha n^\alpha (\mathbf{E} + \mathbf{v}^\alpha \times \mathbf{B}) \cdot \mathbf{v}^\alpha dV + \int_{\mathcal{P}_t^\alpha} (\rho^\alpha \mathbf{b}^\alpha \cdot \mathbf{v}^\alpha + \rho^\alpha r^\alpha + \hat{\varepsilon}^\alpha) dV, \quad (65)$$

where the notation is as before and, additionally, e^α denotes the electric charge per particle of type α .

In comparison with relations (2), (3), and (4) there is an additional contribution of the electromotive force $\mathbf{E} + \mathbf{v}^\alpha \times \mathbf{B}$.

As before we can replace the above equations by their local counterpart in regular points. They have the form

$$m^\alpha \frac{\partial n^\alpha}{\partial t} + m^\alpha \operatorname{div} (n^\alpha \mathbf{v}^\alpha) = \hat{\rho}^\alpha,$$

$$m^\alpha \frac{\partial n^\alpha \mathbf{v}^\alpha}{\partial t} + \operatorname{div} (m^\alpha n^\alpha \mathbf{v}^\alpha \otimes \mathbf{v}^\alpha - \mathbf{T}^\alpha) = e^\alpha n^\alpha (\mathbf{E} + \mathbf{v}^\alpha \times \mathbf{B}) + \rho^\alpha \mathbf{b}^\alpha + \hat{\mathbf{p}}^\alpha,$$

$$m^\alpha \frac{\partial}{\partial t} \left(n^\alpha \varepsilon^\alpha + \frac{1}{2} n^\alpha \mathbf{v}^\alpha \cdot \mathbf{v}^\alpha \right) + \operatorname{div} \left(m^\alpha n^\alpha \left(\varepsilon^\alpha + \frac{1}{2} \mathbf{v}^\alpha \cdot \mathbf{v}^\alpha \right) \mathbf{v}^\alpha + \mathbf{q}^\alpha - \mathbf{T}^\alpha \mathbf{v}^\alpha \right) = \quad (66)$$

$$= e^\alpha n^\alpha \mathbf{v}^\alpha \cdot \mathbf{E} + m^\alpha n^\alpha r^\alpha + m^\alpha n^\alpha \mathbf{b}^\alpha \cdot \mathbf{v}^\alpha + \hat{\varepsilon}^\alpha.$$

The sources must fulfil the conservations laws

$$\sum_{\alpha=1}^A \hat{\rho}^{\alpha} = 0, \quad \sum_{\alpha=1}^A \hat{\mathbf{p}}^{\alpha} = 0, \quad \sum_{\alpha=1}^A \hat{\varepsilon}^{\alpha} = 0. \quad (67)$$

In addition to these thermomechanical balance laws the electromagnetic field must satisfy the Maxwell-Lorentz equations

$$\begin{aligned} \frac{\partial \mathbf{D}}{\partial t} + \mathbf{J} &= \text{rot } \mathbf{H}, \quad (\text{Ampère-Oersted}) \\ \frac{\partial \mathbf{B}}{\partial t} &= -\text{rot } \mathbf{E}, \quad (\text{Faraday}) \\ \text{div } \mathbf{B} &= 0, \quad (\text{Gauss}) \\ \text{div } \mathbf{D} &= e, \quad (\text{Gauss}) \end{aligned} \quad (68)$$

where (*Lorentz aether relations*)

$$\mathbf{D} = \varepsilon_0 \mathbf{E}, \quad \mathbf{B} = \mu_0 \mathbf{H}, \quad e = \sum_{\alpha=1}^A n^{\alpha} e^{\alpha}, \quad \mathbf{J} = \sum_{\alpha=1}^A n^{\alpha} e^{\alpha} \mathbf{v}^{\alpha}. \quad (69)$$

Constants in MKSA (Giorgi) system of units (meter, kg, sec, amper) have the values

$$\begin{aligned} \varepsilon_0 &= 8.854 \times 10^{-12} \frac{A^2 s^4}{kg \, m^3}, \quad \mu_0 = 4\pi \times 10^{-7} \frac{kg \, m}{A^2 s^2}, \\ \varepsilon_0 \mu_0 &= \frac{1}{c^2}, \quad c = 2.99796 \times 10^8 \frac{m}{s}. \end{aligned} \quad (70)$$

This form of Maxwell equations indicates that we neglect any possible structure of molecules and consider them as point charges in vacuum. This assumption, typical for theoretical modeling of gaseous plasmas, is well-supported by experimental evidence in many cases of practical importance – particularly for high temperature plasma. It may not be, however, appropriate for such systems as, for instance, electrolytes or cold metallic vapors where electric polarization of molecules cannot be neglected. An example of this art is the MHD-generator as a pump of liquid metals.

3.3 Bulk equations

We proceed to investigate the bulk equations for the above system. Before we do so let us derive some relations following directly from Maxwell-Lorentz equations.

Taking the divergence of equation (68)₁ and substituting (68)₄ we obtain immediately

$$\frac{\partial e}{\partial t} + \text{div } \mathbf{J} = 0. \quad (71)$$

Hence we obtain the equation of *conservation of charge* and \mathbf{J} is its total flux.

On the other hand, taking the vector product of (68)₁ with \mathbf{B} , we get

$$\varepsilon_0 \frac{\partial \mathbf{E}}{\partial t} \times \mathbf{B} + \mathbf{J} \times \mathbf{B} = \frac{1}{\mu_0} \text{rot } \mathbf{B} \times \mathbf{B} = \frac{1}{\mu_0} [\text{div } (\mathbf{E} \otimes \mathbf{E}) - \frac{1}{2} \text{grad } (\mathbf{B} \cdot \mathbf{B})].$$

Simultaneously

$$\begin{aligned}\varepsilon_0 \frac{\partial \mathbf{E}}{\partial t} \times \mathbf{B} &= \frac{\partial}{\partial t} (\mathbf{D} \times \mathbf{B}) - \varepsilon_0 \mathbf{E} \times \frac{\partial \mathbf{B}}{\partial t} = \\ &= \frac{\partial}{\partial t} (\mathbf{D} \times \mathbf{B}) - \varepsilon_0 \left[\operatorname{div} (\mathbf{E} \otimes \mathbf{E}) - \frac{1}{2} \operatorname{grad} (\mathbf{B} \cdot \mathbf{B}) \right],\end{aligned}$$

where (68)₃ and (68)₄ have been used. Consequently, the combination of these two results yields

$$e\mathbf{E} + \mathbf{J} \times \mathbf{B} = -\frac{\partial \mathbf{D} \times \mathbf{B}}{\partial t} + \operatorname{div} \left[(\mathbf{B} \otimes \mathbf{H} + \mathbf{D} \otimes \mathbf{E}) - \frac{1}{2} (\mathbf{B} \cdot \mathbf{H} + \mathbf{D} \cdot \mathbf{E}) \mathbf{1} \right]. \quad (72)$$

This relation describes the Lorentz force appearing on the left-hand side in terms convenient for conservation laws

The second relation follows when we take the scalar product of (68)₁ with \mathbf{E} . We get

$$\begin{aligned}\mathbf{E} \cdot \mathbf{J} &= \frac{1}{\mu_0} \mathbf{E} \cdot \operatorname{rot} \mathbf{B} = \\ &= -\varepsilon_0 \frac{1}{2} \frac{\partial (\mathbf{E} \cdot \mathbf{E})}{\partial t} + \frac{1}{\mu_0} \operatorname{div} (\mathbf{B} \times \mathbf{E}) + \frac{1}{\mu_0} \mathbf{B} \cdot \operatorname{rot} \mathbf{E} \\ &= -\varepsilon_0 \frac{1}{2} \frac{\partial (\mathbf{E} \cdot \mathbf{E})}{\partial t} + \frac{1}{\mu_0} \operatorname{div} (\mathbf{B} \times \mathbf{E}) - \frac{1}{\mu_0} \frac{1}{2} \frac{\partial (\mathbf{B} \cdot \mathbf{B})}{\partial t}.\end{aligned}$$

Hence

$$\mathbf{E} \cdot \mathbf{J} = -\frac{1}{2} \left(\frac{\partial (\mathbf{D} \cdot \mathbf{E})}{\partial t} + \frac{\partial (\mathbf{B} \cdot \mathbf{H})}{\partial t} \right) - \operatorname{div} (\mathbf{E} \times \mathbf{H}). \quad (73)$$

This is the expression for the Joule heating appearing on the left-hand side convenient for conservation laws.

We are now in the position to formulate the bulk equations for the system. These equations are useful in, at least, two cases. First of all, due to the complexity of the multicomponent system it is very often the case that a one-component model is used. This is the classical magnetohydrodynamics (MHD) for which the multicomponent background is needed only to give the physical inside into different contributions. This classical MHD is frequently applied in the description of wave propagation and stability analysis of plasmas. On the other hand, bulk equations may be used instead of one of the partial equations. We shall do so for the two-component plasma (e.g. for the fully ionized plasmas).

Addition of partial balance equations leads similarly to the mixtures of fluids considered earlier to the following equations

$$\begin{aligned}\frac{\partial \rho}{\partial t} + \operatorname{div} (\rho \mathbf{v}) &= 0, \\ \frac{\partial \rho \mathbf{v}}{\partial t} + \operatorname{div} (\rho \mathbf{v} \otimes \mathbf{v} - \mathbf{T}) &= e\mathbf{E} + \mathbf{J} \times \mathbf{B} + \rho \mathbf{b}, \\ \frac{\partial}{\partial t} \left(\rho \varepsilon + \frac{1}{2} \rho \mathbf{v} \cdot \mathbf{v} \right) + \operatorname{div} \left[\left(\rho \varepsilon + \frac{1}{2} \rho \mathbf{v} \cdot \mathbf{v} \right) \mathbf{v} + \mathbf{q} - \mathbf{T} \mathbf{v} \right] &= \mathbf{E} \cdot \mathbf{J} + \rho r + \rho \mathbf{b} \cdot \mathbf{v},\end{aligned} \quad (74)$$

where

$$\begin{aligned}
\rho &= \sum_{\alpha=1}^A m^{\alpha} n^{\alpha}, \quad \rho \mathbf{v} = \sum_{\alpha=1}^A m^{\alpha} n^{\alpha} \mathbf{v}^{\alpha}, \\
\mathbf{T} &= \sum_{\alpha=1}^A (\mathbf{T}^{\alpha} - m^{\alpha} n^{\alpha} \mathbf{u}^{\alpha} \otimes \mathbf{u}^{\alpha}), \quad \mathbf{u}^{\alpha} = \mathbf{v}^{\alpha} - \mathbf{v}, \quad \rho \mathbf{b} = \sum_{\alpha=1}^A m^{\alpha} n^{\alpha} \mathbf{b}^{\alpha}, \\
\rho \varepsilon &= \sum_{\alpha=1}^A m^{\alpha} n^{\alpha} \left(\varepsilon^{\alpha} + \frac{1}{2} \mathbf{u}^{\alpha} \cdot \mathbf{u}^{\alpha} \right), \\
\mathbf{q} &= \sum_{\alpha=1}^A \left[\mathbf{q}^{\alpha} + m^{\alpha} n^{\alpha} \left(\varepsilon^{\alpha} + \frac{1}{2} \mathbf{u}^{\alpha} \cdot \mathbf{u}^{\alpha} \right) \mathbf{u}^{\alpha} - \mathbf{T}^{\alpha} \mathbf{u}^{\alpha} \right], \\
\rho r &= \sum_{\alpha=1}^A m^{\alpha} n^{\alpha} (r^{\alpha} + \mathbf{b}^{\alpha} \cdot \mathbf{u}^{\alpha}).
\end{aligned} \tag{75}$$

These relations must be combined with the contributions of the electromagnetic field. Bearing the relations (72), (73) in mind we obtain the following final form of the bulk conservation laws

$$\begin{aligned}
&\frac{\partial \rho}{\partial t} + \operatorname{div}(\rho \mathbf{v}) = 0, \\
&\frac{\partial}{\partial t} (\rho \mathbf{v} + \mathbf{D} \times \mathbf{B}) + \\
&+ \operatorname{div}(\rho \mathbf{v} \otimes \mathbf{v} - \mathbf{T} - (\mathbf{B} \otimes \mathbf{H} + \mathbf{D} \otimes \mathbf{E}) + \frac{1}{2} (\mathbf{B} \cdot \mathbf{H} + \mathbf{D} \cdot \mathbf{E}) \mathbf{1}) = \rho \mathbf{b}, \\
&\frac{\partial}{\partial t} \left(\rho \varepsilon + \frac{1}{2} \rho \mathbf{v} \cdot \mathbf{v} + \frac{1}{2} (\mathbf{D} \cdot \mathbf{E} + \mathbf{B} \cdot \mathbf{H}) \right) + \\
&+ \operatorname{div} \left[\left(\rho \varepsilon + \frac{1}{2} \rho \mathbf{v} \cdot \mathbf{v} \right) \mathbf{v} + \mathbf{q} - \mathbf{T} \mathbf{v} + \mathbf{E} \times \mathbf{H} \right] = \rho r + \rho \mathbf{b} \cdot \mathbf{v}.
\end{aligned} \tag{76}$$

In contrast to relations (74) these equations have the divergent form required from true conservation laws. As we see the full momentum density of the mixture is given by $\rho \mathbf{v} + \mathbf{D} \times \mathbf{B}$ and the full energy density by $\rho \varepsilon + \frac{1}{2} \rho \mathbf{v} \cdot \mathbf{v} + \frac{1}{2} (\mathbf{D} \cdot \mathbf{E} + \mathbf{B} \cdot \mathbf{H})$. The corresponding corrections of the momentum flux

$$\mathbf{T}^M = (\mathbf{B} \otimes \mathbf{H} + \mathbf{D} \otimes \mathbf{E}) - \frac{1}{2} (\mathbf{B} \cdot \mathbf{H} + \mathbf{D} \cdot \mathbf{E}) \mathbf{1}, \tag{77}$$

is called the *Maxwell stress tensor*, while the additional flux of energy

$$\mathbf{q}^M = \mathbf{E} \times \mathbf{H}, \tag{78}$$

is called the *Pointing vector*.

Let us now return to the partial mass balance equation. If we multiply this equation by e^α and then perform the summation over all components, we arrive at

$$\frac{\partial e}{\partial t} + \operatorname{div} \mathbf{J} = \sum_{\alpha=1}^A \frac{e^\alpha}{m^\alpha} \hat{\rho}^\alpha. \quad (79)$$

This equation coincides with the conservation of charge (71) if the right-hand side vanishes

$$\sum_{\alpha=1}^A \frac{e^\alpha}{m^\alpha} \hat{\rho}^\alpha = 0. \quad (80)$$

This constraint arises due to the peculiar structure of the mixture which consists of the charged particles.

By means of the partial momentum balance equations we can also derive the equation for the current \mathbf{J} . Multiplying equations (66)₂ by e^α and summing up, we get

$$\begin{aligned} \frac{\partial \mathbf{J}}{\partial t} + \operatorname{div} (\mathbf{J} \otimes \mathbf{v} + \mathbf{v} \otimes \mathbf{J}) - \operatorname{div} \left(e \mathbf{v} \otimes \mathbf{v} + \sum_{\alpha=1}^A \frac{e^\alpha}{m^\alpha} (\mathbf{T}^\alpha - n^\alpha m^\alpha \mathbf{u}^\alpha \otimes \mathbf{u}^\alpha) \right) = \\ = (\mathbf{E} + \mathbf{v} \times \mathbf{B}) \sum_{\alpha=1}^A \frac{(e^\alpha)^2 n^\alpha}{m^\alpha} - \mathbf{B} \times \sum_{\alpha=1}^A \frac{(e^\alpha)^2 n^\alpha}{m^\alpha} \mathbf{u}^\alpha + \sum_{\alpha=1}^A \frac{e^\alpha n^\alpha}{m^\alpha} \mathbf{b}^\alpha + \sum_{\alpha=1}^A \frac{e^\alpha}{m^\alpha} \hat{\mathbf{p}}^\alpha. \end{aligned} \quad (81)$$

This is the most general form of *Ohm's law* which can be derived in the framework of multicomponent MHD model. We return to simplified forms of this equation in the sequel.

3.4 Constitutive relations

In order to get field equations for the fields quoted at the beginning of this Section we have to construct constitutive relations for the following quantities

$$\mathcal{F} = \{\hat{\rho}^\alpha, \mathbf{T}^\alpha, \hat{\mathbf{p}}^\alpha, \varepsilon^\alpha, \mathbf{q}^\alpha, \hat{\varepsilon}^\alpha\}. \quad (82)$$

We shall do so further for a particular case of a two-component system. Little has been done as yet on the basis of the modern thermodynamic approach to the general constitutive problems and such systems as electrolytes, biological fluids were not sufficiently investigated. We make here only a few general remarks on the problem of material objectivity and skip entirely the problem of thermodynamic admissibility.

The main problem in the question of objectivity is the lack of invariance of Maxwell-Lorentz equations even with respect to the Galilean (i.e. time-independent) transformation. This feature of electrodynamics led to the construction of special theory of relativity. It has been shown that these relations are invariant with respect to the change of the so-called Lorentz frames in the space-time. This property indicates rather complicated rules of transformation for fields $\mathbf{E}, \mathbf{D}, \mathbf{H}$ and \mathbf{B} when written in the classical way. However, if we construct the four-dimensional objects

$$(\varphi^{AB}) = \begin{pmatrix} 0 & -E_1 & -E_2 & -E_3 \\ E_1 & 0 & B_3 & -B_2 \\ E_2 & -B_3 & 0 & B_1 \\ E_3 & B_2 & -B_1 & 0 \end{pmatrix}, \quad (\eta^{AB}) = \begin{pmatrix} 0 & D_1 & D_2 & D_3 \\ -D_1 & 0 & H_3 & -H_2 \\ -D_2 & -H_3 & 0 & H_1 \\ -D_3 & H_2 & -H_1 & 0 \end{pmatrix}, \quad (83)$$

then it can be shown that $\boldsymbol{\varphi}$ and $\boldsymbol{\eta}$ are four-tensors. We shall not go into that problem and construct the transformation rules in the classical way.

The starting point for these considerations are assumptions that the *electromotive force*

$$\boldsymbol{\mathcal{E}} = \mathbf{E} + \mathbf{v} \times \mathbf{B}, \quad (84)$$

and the antisymmetric object $\boldsymbol{\Phi}$

$$B_i = \varepsilon_{ijk} \Phi_{jk}, \quad (85)$$

are, respectively, a vector and a tensor of the second rank. These assumptions indicate that the Euclidean transformation provides

$$\boldsymbol{\mathcal{E}}^* = \mathbf{O} \boldsymbol{\mathcal{E}}, \quad \boldsymbol{\Phi}^* = \mathbf{O} \boldsymbol{\Phi} \mathbf{O}^T. \quad (86)$$

Bearing the above remarks in mind, we can write the constitutive variables, for instance, in the following form

$$\mathcal{C} = \{n^\alpha, T^\alpha, \boldsymbol{\mathcal{E}}, \boldsymbol{\Phi}, \mathbf{D}^\alpha, \text{grad } T^\alpha, \mathbf{v}^\alpha - \mathbf{v}^A\}, \quad \mathbf{D}^\alpha = \text{sym grad } \mathbf{v}^\alpha. \quad (87)$$

which describe the compressibility, thermal expansion, electro-magnetic resistivity, viscosity, thermal conductivity, and diffusion, respectively.

It seems that such a general case

$$\mathcal{F} = \mathcal{F}(\mathcal{C}), \quad (88)$$

has never been discussed.

Finally, let us make a remark concerning the structure of source terms. As we know from the thermodynamic theory of fluid mixtures one cannot expect too much from the thermodynamic analysis which may specify the sign but not the detailed structure of these terms. In models of plasma they are usually suggested by some microscopic analysis. In the case of MHD models, one commonly assumes the following form of $\hat{\mathbf{p}}^\alpha$ and $\hat{\varepsilon}^\alpha$ if the mass sources are absent

$$\begin{aligned} \hat{\mathbf{p}}^\alpha &= -n^\alpha m^\alpha \sum_{\beta=1}^A \frac{m^\beta}{m^\alpha + m^\beta} \nu^{\alpha\beta} (\mathbf{v}^\alpha - \mathbf{v}^\beta), \quad \nu^{\alpha\beta} = \nu^{\beta\alpha}, \\ \hat{\varepsilon}^\alpha &= -n^\alpha m^\alpha \sum_{\beta=1}^A \frac{m^\beta}{(m^\alpha + m^\beta)^2} \nu^{\alpha\beta} 3k (T^\alpha - T^\beta), \end{aligned} \quad (89)$$

where $\nu^{\alpha\beta}$ is the collision frequency of α and β - particles and k is the Boltzmann constant. Clearly, it is a very far fetching assumption which ignores all cross effects and nonlinearities. However, it indicates that the momentum source is primarily responsible for the relaxation due to diffusion and the energy source is primarily responsible for the thermal relaxation.

3.5 Two-component model

The simplest mixture of charged particles appears in the case of the fully ionized hydrogen. The mixture contains only electrons and ions of hydrogen. This is a rather hypothetical system because in almost all plasmas which we face there are at least also some neutral particles. However, in order to see some important features of such a multicomponent system we consider now this ideal situation with an additional assumption on the *electric neutrality* $n^e = n^i = n$. Simultaneously

$$\hat{\rho}^e = \hat{\rho}^i = 0, \quad \hat{\mathbf{p}}^e = -\hat{\mathbf{p}}^i := \hat{\mathbf{p}}, \quad \hat{\varepsilon}^e = -\hat{\varepsilon}^i := \hat{\varepsilon}, \quad (90)$$

where, of course, indices e and i denote electrons and ions, respectively.

Fields of the model are as follows

$$\{n, \mathbf{v}^e, \mathbf{v}^i, T^e, T^i, \mathbf{E}, \mathbf{H}\}. \quad (91)$$

It is convenient to make the following transformation of velocity fields

$$(\mathbf{v}^e, \mathbf{v}^i) \rightarrow (\mathbf{v}, \mathbf{J}) \quad (92)$$

where the bulk quantities are defined as follows

$$\begin{aligned} \rho &= m^e n + m^i n \approx m^i n, \\ \rho \mathbf{v} &= m^i n \mathbf{v}^e + m^i n \mathbf{v}^i \rightarrow \mathbf{v} = \mathbf{v}^i + \frac{m^e}{m^i} \mathbf{v}^e, \\ \mathbf{J} &= -en \mathbf{v}^e + en \mathbf{v}^i \rightarrow \frac{1}{en} \mathbf{J} = \mathbf{v}^i - \mathbf{v}^e. \end{aligned} \quad (93)$$

Hence

$$\begin{cases} \mathbf{v}^i = \mathbf{v} + \frac{1}{en} \mathbf{J} \frac{m^e}{m^i}, \\ \mathbf{v}^e = \mathbf{v} - \frac{1}{en} \mathbf{J}, \end{cases} \rightarrow \begin{cases} \mathbf{u}^i = \frac{1}{en} \mathbf{J} \frac{m^e}{m^i}, \\ \mathbf{u}^e = -\frac{1}{en} \mathbf{J}. \end{cases} \quad (94)$$

The set of governing equations has now the following form

$$\begin{aligned} \dot{n} + n \operatorname{div} \mathbf{v} &= 0, \quad \operatorname{div} \mathbf{J} = 0, \quad \dot{n} = \frac{\partial n}{\partial t} + \mathbf{v} \cdot \operatorname{grad} n, \\ \rho \dot{\mathbf{v}} &= \operatorname{div} \mathbf{T} + \mathbf{J} \times \mathbf{B} + \rho \mathbf{b}, \quad \dot{\mathbf{v}} = \frac{\partial \mathbf{v}}{\partial t} + (\mathbf{v} \cdot \operatorname{grad}) \mathbf{v}, \\ \frac{\partial \mathbf{J}}{\partial t} + \operatorname{div} \left(\mathbf{J} \otimes \mathbf{v} + \mathbf{v} \otimes \mathbf{J} - \frac{1}{en} \mathbf{J} \otimes \mathbf{J} + \frac{e}{m^e} \left(\mathbf{T}^e - \frac{m^e}{m^i} \mathbf{T}^i \right) \right) &= \\ &= \frac{e^i n}{m^e} \mathcal{E} - \frac{e}{m^e} \mathbf{J} \times \mathbf{B} - \frac{en}{m^e} (\mathbf{b}^e - \mathbf{b}^i) - \frac{e}{m^e} \hat{\mathbf{p}}, \quad \mathcal{E} = \mathbf{E} + \mathbf{v} \times \mathbf{B}, \\ \varepsilon_0 \frac{\partial \mathbf{E}}{\partial t} + \mathbf{J} &= \frac{1}{\mu_0} \operatorname{rot} \mathbf{B}, \quad \frac{\partial \mathbf{B}}{\partial t} = -\operatorname{rot} \mathbf{E}, \end{aligned} \quad (95)$$

and the following partial energy balance equations

$$\begin{aligned} m^e n \left(\dot{\varepsilon}^e - \frac{1}{en} \mathbf{J} \cdot \operatorname{grad} \varepsilon^e \right) &= \mathbf{T}^e \cdot \operatorname{grad} \mathbf{v} - \mathbf{T}^e \cdot \operatorname{grad} \frac{1}{en} \mathbf{J} - \\ &\quad - \operatorname{div} \mathbf{q}^e + m^e n r^e + \hat{\varepsilon} - \mathbf{v} \cdot \hat{\mathbf{p}} + \frac{1}{en} \mathbf{J} \cdot \hat{\mathbf{p}}, \end{aligned}$$

$$\begin{aligned}
m^i n \left(\dot{\varepsilon}^i + \frac{1}{en} \mathbf{J} \cdot \text{grad} \varepsilon^i \frac{m^e}{m^i} \right) &= \mathbf{T}^i \cdot \text{grad} \mathbf{v} + \mathbf{T}^i \cdot \text{grad} \frac{1}{en} \mathbf{J} \frac{m^e}{m^i} - \\
&\quad - \text{div} \mathbf{q}^e + m^i n r^i - \hat{\varepsilon} + \mathbf{v} \cdot \hat{\mathbf{p}} + \frac{1}{en} \mathbf{J} \cdot \hat{\mathbf{p}} \frac{m^e}{m^i}.
\end{aligned} \tag{96}$$

Certainly, we still need constitutive relations in order to close the system. In most cases of practical importance, it is assumed that they have the form of constitutive laws for an ideal gas, e.g.

$$\begin{aligned}
\mathbf{T}^e &= -p^e \mathbf{1}, & \mathbf{T}^i &= -p^i \mathbf{1}, \\
m^e n \varepsilon^e &= \frac{3}{2} p^e, & m^i n \varepsilon^i &= \frac{3}{2} p^i,
\end{aligned} \tag{97}$$

Under these assumptions some estimates of relaxation times, stability properties, etc. have been solved. For instance, the typical relaxation time for thermal processes (equal temperatures of components!) have been estimated for hydrogen to be of the order of $10^{-3} s$.

For further details we refer the reader to the literature on plasma physics.

4 Porous materials as mixtures – phenomenology

4.1 Diffusion and thermodiffusion in systems with a solid phase

Theories of porous and granular materials can be constructed on different levels of observation. *Microscopic* models rely on Newton equations of motion of material points or molecules and use methods of molecular dynamics. Such models can be transferred on a *semimacroscopic* level by multiscaling and averaging procedures. Finally, on a *macroscopic* level continuous field models are constructed. These may either follow from semi-macroscopic models by homogenizing, averaging over Representative Elementary Volumes (REV), construction of moments of kinetic distribution functions or they may be constructed by means of a phenomenological macroscopic approach. In these notes we present solely the latter type of models with a marginal reference to averaging procedures.

The construction of macroscopic continuous models of systems with a solid component in its most sophisticated form stems from models of multicomponent systems. Differences are primarily connected with an art of interactions within the solid component. Models must be clearly different in the cases of suspensions, of granular materials or of porous materials. In the first case solid particles interact with each other either through the fluid or through collisions and there is no permanent contact between them. In the second case a granular solid component may behave as a solid which cannot carry a tensile loading (unilateral constraint on constitutive relations) or it may fluidize and then behave as a suspension. Finally a porous material behaves in average as a usual solid and it forms a deformable carrier for fluid components. We limit our attention in these notes to the last case.

The most important feature of *porous materials* is the appearance of different kinematics for the solid component - the *skeleton*, and fluid components in channels of the skeleton. This yields *diffusion processes* characterized by relative velocities of components. In most cases of a practical bearing the dependence on the relative velocity is reduced to a linear contribution to momentum balance equations (momentum sources) or even to a simpler form called the *Darcy law*. In these notes we present solely some elements of a more general approach which leads to a set of hyperbolic field equations reminding the hierarchy appearing in the extended thermodynamics [60], [63]. Some details can be found in references quoted in the sequel.

The problem of *thermodiffusion* within such models is still very much open. This is related to difficulties with an appropriate definition of the temperature on the macroscopic level of description. The most important property of the classical *thermodynamical temperature*, its continuity on ideal thermal walls and, consequently, its experimental measurability, is not fulfilled in porous materials ([52], p. 76). In addition such processes as phase transitions or chemical reactions in porous materials are characterized by real thermodynamical temperatures (e.g. melting and freezing points, evaporation, etc.) of components on a semimacroscopic level of description. It means that even if we have introduced a macroscopic notion of temperature we would have to know a rule of transformation of this quantity to the semimacroscopic level. This is mathematically an ill-posed problem. Even though one can formally work with notions such as partial heat fluxes, specific heats etc. their operational meaning is not clarified yet. This seems to be one of the most important open issues of modelling porous and granular materials.

In addition we have to deal frequently with the problem of different temperatures for different components. In contrast to gases a local thermodynamical equilibrium is reached in porous and granular materials after macroscopically long relaxation times. For instance a hot water flowing through a cold porous material does not reach locally a common temperature with the skeleton within seconds or minutes. Consequently we should construct thermodynamical models with different temperatures of components. Such a construction is missing even in the case of fluid mixtures. One of the reasons is again the problem of measurability.

Let us mention in passing that in theories of granular materials stemming from a kinetic equation it is common to work with a *kinetic temperature* rather than a thermodynamical temperature. It is defined in a way similar to this of the kinetic theory of gases as a mean kinetic energy of granulae. There are numerous difficulties connected with such a notion. For example a natural equilibrium state of a granular material in which particles do not move would have a temperature equal to zero. Consequently deviations from the equilibrium state which are used in the construction of macroscopic moment equations of the kinetic theory would have to be constructed by means of a trivial distribution function. Certainly this cannot give any reasonable physical results. For this reason moment equations are constructed by a reference to a Maxwell-like distribution describing processes of simple shearing flows rather than real equilibrium states. In contrast to - say - Grad 13 moment method of rarified gases such procedures are not justified in any way. Moreover the questions of measurability of kinetic temperature, a relation to the thermodynamical temperature etc. are not even asked as yet.

4.2 Mass exchange, chemical reactions, adsorption

Within multicomponent continuous models an exchange of mass is described by mass sources in partial mass balance equations. However these contributions must contain additional *microstructural* variables. For instance in the case of chemical reactions this is the vector of extent of chemical reaction (e.g. [34], [45]). This requires an extension of the set of field equations. In many cases additional equations for microstructural variables have the form of evolution equations. Then there is no need to introduce additional boundary conditions. Such microstructural variables cannot be controlled, they develop spontaneously from initial data. On the other hand the latter can be usually easily formulated because many microstructural variables are defined in such a way that they vanish in thermodynamical equilibria.

Further in these notes we present in some details a model of processes of exchange of mass called *adsorption*. These processes appear in cases of components which, in contrast to chemical bindings, form weak van der Waals bindings solely with the skeleton. Such are, for example, processes of transport of many pollutants in soils. According to the simplest model of these processes, developed by Langmuir (see: [62], [1], [2], [3] for references) they are described by an additional field of the so-called number of bare sites. In the case of materials with very small diameters of channels adsorption processes possess a hysteresis loop in the relation between the partial pressure of adsorbate in the fluid phase and an amount of mass adsorbed by the skeleton and this plays a very important role in controlling technological processes in such materials. Such loops are caused by capillary effects. For this reason they do not appear in materials with moderate and large channels

which is characteristic for usual soils.

4.3 Dynamics; additional modes of bulk and surface waves

As already mentioned above multicomponent models of porous materials contain more than one velocity field. This yields field equations following from partial momentum balance equations with a corresponding number of partial accelerations. Consequently one expects that in such models additional modes of weak discontinuity waves have to appear. This is indeed the case. One of these modes was predicted by M. A. Biot in 1941 (see the collection of Biot's papers on porous materials [43]). Due to the tradition stemming from geophysics this mode is called P2 compressional (Biot's) wave as the usual longitudinal wave registered in seismograms was called P1. Existence of this mode was confirmed in numerous experiments. It has been found out that it is the slowest of three modes P1, S (transversal wave) and P2. It is also very strongly attenuated.

As consequence of existence of additional modes there exist as well additional modes of surface waves. Apart from the classical Rayleigh wave there exist the so-called Stoneley waves, various leaky waves and, in general, a number of possible modes of surface waves depends on properties of neighboring systems, i.e. on the structure of boundary conditions. We discuss this problem further in these notes. Let us mention that surface waves are much weaker attenuated as bulk waves and for this reason they are easier attainable in measurements. In recent years one can observe a vehement progress in these measuring techniques (see [31] for some recent reviews and references).

4.4 Coupled problems (combustion, explosions)

Couplings of dynamical properties of porous and granular materials with mass exchange between components play an important role in various combustion and explosion problems. These are connected with the propagation of strong discontinuities such as shock waves and combustion fronts in combustion of solid fuels or deformations of soils due to impacts of meteorites. Models for such processes are still rather weakly developed. Most important contributions are based on the model proposed by M. A. Goodman and C. Cowin [23] (see also [38]) which refers to some additional microstructural properties called the principle of equilibrated pressures. The model leads to a quasilinear hyperbolic set of equations which admits the existence of shock waves. However, apart from some rather simple properties of propagation conditions results are rather scarce.

Some elementary properties of one-dimensional Rankine-Hugoniot conditions have been also investigated within the frame of the model with the porosity balance equation. However a comprehensive theory of shock waves is still missing and one of the reasons is lack of a selection (entropy) criterion.

4.5 Instabilities (e.g. eruptions during earthquakes)

Many processes in porous and granular materials are connected with the development of instabilities. They lead to fluidization of saturated sands, to the creation of patterns in porous materials and to some instabilities, such as Saffmann-Taylor, in flows of fluid components. As usual they are connected with nonlinearities appearing in the model.

One of the most spectacular phenomena accompanying earthquakes is the fountain-like explosion of water from the sand. It has been found that prior to this phenomenon the character of permeability of the soil changes in an unstable manner. In the first stage the homogeneity of the system breaks down and a pattern of chimney-like channels with a very high permeability is formed. In the second stage one of these channels becomes dominant and this leads to an explosion-like eruption of water from the ground. This behavior seems to be connected with a nonlinear coupling of the diffusion velocity with the gradient of porosity.

Another class of instabilities appears in the model with the balance equation of porosity. These are connected with the coupling between dynamical changes of porosity and partial stresses in components. Let us mention one of those instabilities. In a case of a Riemann problem the system develops soliton-like waves of porosity [39]. These are connected with the loss of symmetry of the front of propagation if the two-dimensional front is concave. Most likely in the vicinity of the symmetry axis the system develops a mushy region.

4.6 Subjects considered in these notes

Further we present a series of models of porous materials and we concentrate on their formal structure rather than on practical applications.

We begin with the presentation of some aspects of models in which changes of porosity, the microstructural variable characteristic for porous materials, are described by partial mass balance equations. This is possible under the assumption that real components are incompressible (see: [61], [51] for further details).

The next model considered contains all fundamental fields characteristic for porous materials and changes of porosity are described by its own balance equation. Such an equation can be formulated in different forms. We concentrate in this notes on a single choice of the equation of the first order [53], [54], [55], [57] and do not discuss other possibilities. The purpose of this model is primarily to show that, at least in some cases, the thermodynamic construction of models of porous materials can be done by means of methods developed within the so-called rational extended thermodynamics [35].

The subsequent model is constructed on the basis of the classical thermodynamic approach and demonstrates that the dependence on the gradient of porosity as the constitutive variable yields models with couplings appearing, for instance, in the linear model constructed by M. Biot and considered to be the reference for models of porous materials. If we neglect this dependence we obtain a model which corresponds to the model of simple mixtures of fluids discussed earlier. In this Section the model is based on constitutive assumptions for changes of porosity [66] but the conclusions can be easily extended on a model with the balance equation of porosity which we do not show in these notes (e.g. compare: [69]).

As next we present the model in which we include two effects: dependence on the temperature gradient and on the relative acceleration of components (see: [72] for details). The latter is sometimes contributed to the influence of the so-called tortuosity on the behavior of porous materials (e.g. [10], [16], [27]). Tortuosity is the microstructural property describing the relation of the real length of streamlines of fluid components to the macroscopic distance or, if the channels in the skeleton are well-defined geometrical

objects, the ratio of the length of such channels to the macroscopic length. Consequently, the variable describing this effect is a scalar bigger than one. It is rather doubtful if indeed the relative acceleration as a constitutive variable corresponds to the tortuosity but the dependence seems to indicate the existence of some other nonlinear effects which are related to the added mass effect.

All models mentioned above are nonlinear. In cases of large deformations of the skeleton we use the Lagrangian description [52].

In the subsequent Section we discuss a certain linear extension of Biot's model and Biot's model itself. The main purpose of this discussion is to show the determination of some effective (macroscopic) material parameters by means of properties of real components. This yields the so-called Gassmann-type relations [70].

Finally we show some properties of acoustic waves in linear poroelastic materials. This example of application of the linear models has an important practical bearing in nondestructive testing and in seismology [31].

5 Some models of porous materials with the incompressibility assumption

Multicomponent modeling of porous materials is based on the assumption that additionally to usual fields of theories of fluid mixtures there exists a microstructure which is reflected in the simplest case by a single additional field of porosity and by solid-like properties of one of the components. In some models this microstructural extension is even broader and corresponding models contain, for instance, the so-called volume fractions of all components, double porosity, tortuosity as a simplest measure of complexity of geometrical structure of channels, couple stresses etc.

We present in this Section an example of such a model for a two-component system with an assumption of incompressibility of components. Models of this art appear quite frequently in applications to soil mechanics or glaciology [49].

As in all continuum models we define in *Eulerian description* fields on a common domain \mathcal{B}_t which is time dependent and corresponds to a part of the three-dimensional space of motion occupied in a current instant of time by all components. In the case of semipermeable boundary $\partial\mathcal{B}_t$ parts of components which flow out of this domain are considered separately and one has to solve contact problems. We return to the problem of configurations of multicomponent system further in this work.

In a purely mechanical model which we want to consider in this Section processes are described by two current partial mass densities $\rho_t^S(\mathbf{x}, t), \rho_t^F(\mathbf{x}, t), \mathbf{x} \in \mathcal{B}_t \subset \mathfrak{R}^3, t \in \mathcal{T} \subset \mathfrak{R}$, for the skeleton and the fluid component, respectively, and by two velocity fields $\mathbf{v}^S(\mathbf{x}, t), \mathbf{v}^F(\mathbf{x}, t)$ for these two components. All these fields are *macroscopic* which means that they are defined on the common domain \mathcal{B}_t and, for instance the fluid mass and the skeleton mass contained in a subdomain $\mathcal{P}_t \subset \mathcal{B}_t$ are given by the Lebesgue integrals

$$M^F(\mathcal{P}_t) = \int_{\mathcal{P}_t} \rho_t^F dV, \quad M^S(\mathcal{P}_t) = \int_{\mathcal{P}_t} \rho_t^S dV. \quad (98)$$

In the definition of incompressible components one uses a "pseudomesoscopic" quantities which are called *realistic mass densities*. We denote them by ρ_t^{SR} and ρ_t^{FR} . They are also defined in each point of the domain \mathcal{B}_t and not in points of the skeleton or of the fluid, respectively. They may be related to mesoscopic (or semimacroscopic) quantities ρ_m^{SR}, ρ_m^{FR} by the following formulae

$$\rho_t^{SR} = \frac{1}{V(\mathcal{P}_t^S)} \int_{\mathcal{P}_t} \rho_m^{SR} (1 - H^F) dV, \quad \rho_t^{FR} = \frac{1}{V(\mathcal{P}_t^F)} \int_{\mathcal{P}_t} \rho_m^{FR} H^F dV, \quad (99)$$

where

$$\begin{aligned} \mathcal{P}_t &= \mathcal{P}_t^S \cup \mathcal{P}_t^F, \quad \mathcal{P}_t^S \cap \mathcal{P}_t^F = \emptyset, \\ V(\mathcal{P}_t^F) &:= \int_{\mathcal{P}_t} H^F dV, \quad V(\mathcal{P}_t^S) := \int_{\mathcal{P}_t} (1 - H^F) dV, \end{aligned} \quad (100)$$

and H^F is the characteristic function for \mathcal{P}_t^F . \mathcal{P}_t is a neighborhood of a generic point \mathbf{x} and it is usually chosen to be identical for all points of the porous body, i.e. it is obtained by a shift of a chosen domain over the whole current configuration \mathcal{B}_t . This domain should be small enough to deliver a good approximation, for instance, in the

vicinity of the boundary. Then it is called the *Representative Elementary Volume (REV)*. In contrast to ρ_t^{SR}, ρ_t^{FR} which do not possess any physical interpretation in points of the real fluid for the first quantity and in points of the skeleton for the second one, the mass densities ρ_m^{SR}, ρ_m^{FR} are defined solely in points of the real skeleton, and of the real fluid, respectively. Consequently, they possess a usual physical interpretation. For instance, ρ_m^{FR} is equal to $1000 \frac{kg}{m^3}$ for water in normal conditions.

It is easy to check the following relations

$$V(\mathcal{P}_t^S) = (1 - n) V(\mathcal{P}_t), \quad V(\mathcal{P}_t^F) = n V(\mathcal{P}_t), \quad (101)$$

$$n := \frac{1}{V(\mathcal{P}_t)} \int_{\mathcal{P}_t} H^F dV, \quad V(\mathcal{P}_t) := \int_{\mathcal{P}_t} dV.$$

The quantity n defined in (101)₃ is called the *porosity*.

Consequently

$$\begin{aligned} \rho_t^S &: = \frac{1}{V(\mathcal{P}_t)} \int_{\mathcal{P}_t} \rho_m^{SR} (1 - H^F) dV = (1 - n) \rho_t^{SR}, \\ \rho_t^F &: = \frac{1}{V(\mathcal{P}_t)} \int_{\mathcal{P}_t} \rho_m^{FR} H^F dV = n \rho_t^{FR}. \end{aligned} \quad (102)$$

Clearly, the smeared-out, partial mass densities ρ_t^S, ρ_t^F are related to the common macroscopic volume in the current configuration. Their definitions contain the full volume of REV.

By means of the above relations we are now in the position to introduce the notion of incompressibility appearing in some theories of porous and granular materials. Namely it is assumed for such models that

$$\rho_t^{SR} = const., \quad \rho_t^{FR} = const. \quad (103)$$

Consequently the current mass densities ρ_t^F, ρ_t^S are not independent fields. They can be reduced to the single field of porosity n . In such a case partial mass balance equations (without mass exchange!) reduce to the following form

$$\begin{aligned} \frac{1}{\rho_t^{SR}} \left\{ \frac{\partial \rho_t^S}{\partial t} + \operatorname{div}(\rho_t^S \mathbf{v}^S) \right\} &\equiv -\frac{\partial n}{\partial t} + \operatorname{div}((1 - n) \mathbf{v}^S) = 0, \\ \frac{1}{\rho_t^{FR}} \left\{ \frac{\partial \rho_t^F}{\partial t} + \operatorname{div}(\rho_t^F \mathbf{v}^F) \right\} &\equiv \frac{\partial n}{\partial t} + \operatorname{div}(n \mathbf{v}^F) = 0. \end{aligned} \quad (104)$$

We can also combine these two equations to the following one

$$\operatorname{div}(n \mathbf{v}^F + (1 - n) \mathbf{v}^S) = 0. \quad (105)$$

If we consider equation (104)₁ as a candidate for the field equation for the porosity n then equation (105) is a *constraint condition* of the model. This condition yields certain limitations on constitutive relations appearing in the phenomenological model which are not always physically and mathematically acceptable (see: [12]). We show here two

examples of models which are thermodynamically admissible. The first one is used frequently in soil mechanics and in the description of suspensions. In order to obtain field equations we need momentum balance equations which have the following form in the Eulerian description

$$\begin{aligned} \frac{\partial (\rho_t^S \mathbf{v}^S)}{\partial t} + \operatorname{div} (\rho_t^S \mathbf{v}^S \otimes \mathbf{v}^S - \mathbf{T}^S) &= \hat{\mathbf{p}}^S, \\ \frac{\partial (\rho_t^F \mathbf{v}^F)}{\partial t} + \operatorname{div} (\rho_t^F \mathbf{v}^F \otimes \mathbf{v}^F - \mathbf{T}^F) &= \hat{\mathbf{p}}^F, \quad \hat{\mathbf{p}}^S + \hat{\mathbf{p}}^F = 0, \end{aligned} \quad (106)$$

where $\mathbf{T}^S, \mathbf{T}^F$ denote symmetric partial Cauchy stress tensors, $\hat{\mathbf{p}}^S, \hat{\mathbf{p}}^F$ are momentum sources. We make the assumption that these quantities satisfy the following constitutive relations

$$\begin{aligned} \mathbf{T}^S &= \mathbf{T}^S(n, \operatorname{grad} n, \mathbf{e}^S, \mathbf{w}), \quad \mathbf{T}^F = \mathbf{T}^F(n, \operatorname{grad} n, \mathbf{e}^S, \mathbf{w}), \\ \hat{\mathbf{p}}^S &= \hat{\mathbf{p}}^S(n, \operatorname{grad} n, \mathbf{e}^S, \mathbf{w}), \end{aligned} \quad (107)$$

where the symmetric deformation tensor of the skeleton \mathbf{e}^S satisfies for small deformations¹ the equation

$$\frac{\partial \mathbf{e}^S}{\partial t} = \operatorname{sym} \operatorname{grad} \mathbf{v}^S, \quad (108)$$

and $\mathbf{w} := \mathbf{v}^F - \mathbf{v}^S$ is the relative velocity of components.

By means of the second law of thermodynamics one can show that the constraint (105) is thermodynamically admissible. This would not be the case were constitutive relations (107) independent of $\operatorname{grad} n$ [61]. In this sense we deal with a *higher gradient model*. If we assume in addition the isotropy and linearity with respect to both vector variables $\operatorname{grad} n$ and \mathbf{w} then we obtain a relatively explicit form of constitutive relations

$$\begin{aligned} \mathbf{T}^S &= -(1-n)p\mathbf{1} + \mathbf{T}_{eff}^S(n, \mathbf{e}^S), \quad \mathbf{T}^F = -np\mathbf{1} + \mathbf{T}_{eff}^F(n, \mathbf{e}^S), \\ \hat{\mathbf{p}}^S &= -\hat{\mathbf{p}}^F = \pi(n, \mathbf{e}^S) \mathbf{w} - p \operatorname{grad} n, \end{aligned} \quad (109)$$

where $\mathbf{T}_{eff}^S, \mathbf{T}_{eff}^F$ are the so-called *effective partial stress tensors*. The second one is frequently assumed to be zero and the first one, if it is linear (small deformation of the skeleton $\|\mathbf{e}^S\| \ll 1$), is given by a Hooke's law with material coefficients depending on the porosity n . The *permeability coefficient* π is also usually assumed to be constant. The *pore pressure* p is the reaction force on the constraint.

In order to account for instabilities of the microstructure one can try to extend the above model by accounting for nonlinear dependence on the relative velocity \mathbf{w} . This is justified because such instabilities appear by flows of a high intensity of the fluid component. In a continuum model the latter corresponds to contributions $\rho_t^F \mathbf{w}$. Such an extension yields in the lowest approximation the following constitutive relations

$$\begin{aligned} \mathbf{T}^S &= -(1-n)p\mathbf{1} + \mathbf{T}_{eff}^S(n, \mathbf{e}^S) + \delta \mathbf{w} \otimes \mathbf{w}, \\ \mathbf{T}^F &= -np\mathbf{1} + \mathbf{T}_{eff}^F(n, \mathbf{e}^S) - \delta \mathbf{w} \otimes \mathbf{w}, \end{aligned} \quad (110)$$

¹i.e. $\|\mathbf{e}^S\| \ll 1$, where $\|\mathbf{e}^S\| = \max \{\lambda^{(1)}, \lambda^{(2)}, \lambda^{(3)}\}$ and $\lambda^{(1)}, \lambda^{(2)}, \lambda^{(3)}$ are eigenvalues of \mathbf{e}^S .

$$\hat{\mathbf{p}}^S = -\hat{\mathbf{p}}^F = \pi(n, \mathbf{e}^S) \mathbf{w} - (p + \Gamma \mathbf{w} \cdot \mathbf{w}) \operatorname{grad} n,$$

where δ and Γ are additional material parameters.

Such a model seems to be appropriate to describe, for instance, instabilities leading to fluidization and eruption in water saturated sands by earthquakes ([51], ²).

The above described class of models shall not be discussed any further in this work. In spite of their important role in some problems of soil mechanics these models have some faults which do not seem to be acceptable in cases of wave processes. Most important of them is the lack of hyperbolicity (the part of the operator connected with the constraint is elliptic). This leads to a reduced number of real eigenvalues corresponding to speeds of propagation and, consequently, to the lack of certain modes of propagation of weak discontinuity waves. In particular the P2-wave and some important surface waves cannot be described by such models. We discuss the structure of those modes following from a different model presented further in these notes.

²see also: the PhD Thesis of Theo Wilhelm at the University of Innsbruck, Institut für Geotechnik und Tunnelbau of Prof. D. Kolymbas

6 The model with the porosity balance equation and extended thermodynamics

In this Section we present the model of porous materials developed in the recent years [56] for an elastic skeleton and ideal fluid components. We present its nonlinear foundations for a system with A fluid components. Only a few basic thermodynamical features will be discussed in order to place the model within the rational extended thermodynamics [60], [68]. Thermodynamical details will be discussed in further Sections for two-component models.

Geometric nonlinearities connected with possibly large deformations of the skeleton indicate that the convenient way to describe processes is to define fields on a *reference configuration* \mathcal{B}_0 of the skeleton. For such a configuration the deformation gradient of the skeleton is defined as the unit matrix: $\mathbf{F}^S = \mathbf{1}$. Hence we formulate the *Lagrangian description* of motion of the porous material.

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

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

Consequently a *thermomechanical process* is described by the mapping

$$\mathbf{u} : (\mathbf{X}, t) \mapsto \mathbb{R}^{4A+15}, \quad \mathbf{u} := \{\rho^S, \rho^\alpha, \dot{\mathbf{x}}^S, \mathbf{F}^S, \dot{\mathbf{x}}^\alpha, n, T\}, \quad \alpha = 1, \dots, A. \quad (111)$$

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

Balance equations are formulated in their global form on material domains of components. For porous materials in the Lagrangian description the family of material domains for the skeleton is defined as a class of subsets of \mathcal{B}_0 which is time independent and satisfies conditions identical with those of the classical continuum mechanics (e.g. [44]). Material domains of the skeleton are time independent because the reference configuration \mathcal{B}_0 is defined with respect to the deformation gradient of skeleton \mathbf{F}^S . For this configuration $\mathbf{F}^S = \mathbf{1}$.

It is not the case any more for fluid components. They have different kinematics than the skeleton which means that domains in the space of motion containing during the motion the same particles of a particular fluid component move with respect to material domains of the skeleton. In the Eulerian description the velocity field for this motion is

given by the difference $\mathbf{v}^\alpha(\mathbf{x}, t) - \mathbf{v}^S(\mathbf{x}, t)$ for the fluid component α , where $\mathbf{v}^\alpha(\mathbf{x}, t)$ is the velocity of the fluid and $\mathbf{v}^S(\mathbf{x}, t)$ is the velocity of the skeleton at the same spatial position \mathbf{x} and at the same instant of time t . This relative motion yields the time dependence of material domains of fluid components projected on the reference configuration \mathcal{B}_0 . The projection is carried by the function of motion of the skeleton

$$\begin{aligned} \forall \mathbf{X} \in \mathcal{B}_0, t \in \mathcal{T} : \quad \mathbf{x} = \boldsymbol{\chi}^S(\mathbf{X}, t) &\implies \\ \implies \mathbf{F}^S = \text{Grad } \boldsymbol{\chi}^S(\mathbf{X}, t), \quad \dot{\mathbf{x}}^S = \frac{\partial \boldsymbol{\chi}^S(\mathbf{X}, t)}{\partial t}, \end{aligned} \quad (112)$$

whose existence is assumed in the model. The condition for the existence of the function of motion $\boldsymbol{\chi}^S$ shall be formulated later.

It is easy to check that the Lagrangian fields of velocities of material domains of fluid components are given by the following relation

$$\begin{aligned} \forall \mathbf{X} \in \mathcal{B}_0 : \quad \dot{\mathbf{X}}^\alpha(\mathbf{X}, t) &:= \mathbf{F}^{S-1}(\dot{\mathbf{x}}^\alpha - \dot{\mathbf{x}}^S), \\ \dot{\mathbf{x}}^S(\mathbf{X}, t) &= \mathbf{v}^S(\boldsymbol{\chi}^S(\mathbf{X}, t), t), \quad \dot{\mathbf{x}}^\alpha(\mathbf{X}, t) = \mathbf{v}^\alpha(\boldsymbol{\chi}^S(\mathbf{X}, t), t). \end{aligned} \quad (113)$$

In order to appreciate the operational meaning of this transformation we formulate balance equations of mass for all components. They have the following form

$$\frac{d}{dt} \int_{\mathcal{P}^S} \rho^S dV = \int_{\mathcal{P}^S} \hat{\rho}^S dV, \quad (114)$$

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

$$\frac{d}{dt} \int_{\mathcal{P}^\alpha(t)} \rho^\alpha dV = \int_{\mathcal{P}^\alpha(t)} \hat{\rho}^\alpha dV, \quad (115)$$

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

$$\forall \mathbf{X} \in \mathcal{B}_0, t \in \mathcal{T} : \quad \hat{\rho}^S + \sum_{\alpha=1}^A \hat{\rho}^\alpha = 0. \quad (116)$$

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

$$\begin{aligned} \frac{d}{dt} \int_{\mathcal{P}^S} \rho^S dV &= \int_{\mathcal{P}^S} \frac{\partial}{\partial t} \rho^S dV, \\ \frac{d}{dt} \int_{\mathcal{P}^\alpha(t)} \rho^\alpha dV &= \int_{\mathcal{P}^\alpha(t)} \frac{\partial}{\partial t} \rho^\alpha dV + \oint_{\partial \mathcal{P}^\alpha(t)} \rho^\alpha \mathbf{N} \cdot \dot{\mathbf{X}}^\alpha dS, \end{aligned} \quad (117)$$

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

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

$$\frac{\partial \rho^S}{\partial t} = \hat{\rho}^S, \quad \frac{\partial \rho^\alpha}{\partial t} + \text{Div} \left(\rho^\alpha \dot{\mathbf{X}}^\alpha \right) = \hat{\rho}^\alpha, \quad (118)$$

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

$$U \left[[\rho^S] \right] = 0, \quad \left[\left[\rho^\alpha \left(\dot{\mathbf{X}}^\alpha \cdot \mathbf{N} - U \right) \right] \right] = 0, \quad (119)$$

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

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

$$\begin{aligned} \frac{\partial (\rho^S \dot{\mathbf{X}}^S)}{\partial t} - \text{Div} \mathbf{P}^S &= \hat{\mathbf{p}}^S + \rho^S \mathbf{b}^S, \\ \frac{\partial (\rho^\alpha \dot{\mathbf{X}}^\alpha)}{\partial t} + \text{Div} \left(\rho^\alpha \dot{\mathbf{X}}^\alpha \otimes \dot{\mathbf{X}}^\alpha - \mathbf{P}^\alpha \right) &= \hat{\mathbf{p}}^\alpha + \rho^\alpha \mathbf{b}^\alpha, \quad \hat{\mathbf{p}}^S + \sum_{\alpha=1}^A \hat{\mathbf{p}}^\alpha = 0, \end{aligned} \quad (120)$$

and for points on singular surfaces

$$\begin{aligned} \rho^S U \left[[\dot{\mathbf{X}}^S] \right] + \left[[\mathbf{P}^S] \right] \mathbf{N} &= 0, \\ \rho^\alpha \left(\dot{\mathbf{X}}^\alpha \cdot \mathbf{N} - U \right) \left[[\dot{\mathbf{X}}^\alpha] \right] - \left[[\mathbf{P}^\alpha] \right] \mathbf{N} &= 0. \end{aligned} \quad (121)$$

In these relations $\mathbf{P}^S, \mathbf{P}^\alpha$ denote partial Piola-Kirchhoff stress tensors, $\mathbf{b}^S, \mathbf{b}^\alpha$ are partial mass forces, and $\hat{\mathbf{p}}^S, \hat{\mathbf{p}}^\alpha$ denote the momentum sources. Relation (120)₃ expresses the bulk conservation of momentum.

We do not need to present details of partial energy balance equations. Under the assumption of a single field of temperature we need solely the bulk energy conservation law. Details concerning partial energy balance equations and the derivation of the bulk equation can be found in the book [56]. The derivation is based on a principle of the theory of mixtures that bulk quantities must be defined in such a way that balance equations for these quantities have the form of classical conservation laws of the single component continuum thermodynamics.

Bearing this principle in mind we define the following bulk quantities

$$\rho := \rho^S + \sum_{\alpha=1}^A \rho^\alpha, \quad \rho \dot{\mathbf{X}} := \rho^S \dot{\mathbf{X}}^S + \sum_{\alpha=1}^A \rho^\alpha \dot{\mathbf{X}}^\alpha, \quad \rho \dot{\mathbf{X}} := \sum_{\alpha=1}^A \rho^\alpha \dot{\mathbf{X}}^\alpha, \quad (122)$$

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

$$\begin{aligned} \mathbf{P} &: = \mathbf{P}_I - \mathbf{F}^S \left\{ \rho^S \dot{\mathbf{X}} \otimes \dot{\mathbf{X}} + \sum_{\alpha=1}^A \rho^\alpha \left(\dot{\mathbf{X}}^\alpha - \dot{\mathbf{X}} \right) \otimes \left(\dot{\mathbf{X}}^\alpha - \dot{\mathbf{X}} \right) \right\}, \\ \mathbf{P}_I &: = \mathbf{P}^S + \sum_{\alpha=1}^A \mathbf{P}^\alpha; \end{aligned} \quad (123)$$

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

$$\begin{aligned}\rho\varepsilon &: = \rho\varepsilon_I + \frac{1}{2} \left\{ \rho^S \mathbf{C}^S \cdot (\dot{\mathbf{X}} \otimes \dot{\mathbf{X}}) + \sum_{\alpha=1}^A \rho^\alpha \mathbf{C}^S \cdot (\dot{\mathbf{X}}^\alpha - \dot{\mathbf{X}}) \otimes (\dot{\mathbf{X}}^\alpha - \dot{\mathbf{X}}) \right\}, \\ \rho\varepsilon_I &: = \rho^S \varepsilon^S + \sum_{\alpha=1}^A \rho^\alpha \varepsilon^\alpha, \quad \mathbf{C}^S := \mathbf{F}^{ST} \mathbf{F}^S,\end{aligned}\tag{124}$$

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

$$\begin{aligned}\mathbf{Q} &:= \mathbf{Q}_I + \frac{1}{2} \left\{ -\rho^S \dot{\mathbf{X}} \otimes \dot{\mathbf{X}} \otimes \dot{\mathbf{X}} + \sum_{\alpha=1}^A \rho^\alpha (\dot{\mathbf{X}}^\alpha - \dot{\mathbf{X}}) \otimes (\dot{\mathbf{X}}^\alpha - \dot{\mathbf{X}}) \otimes (\dot{\mathbf{X}}^\alpha - \dot{\mathbf{X}}) \right\} \mathbf{C}^S, \\ \mathbf{Q}_I &: = \mathbf{Q}^S + \sum_{\alpha=1}^A \mathbf{Q}^\alpha - \rho^S \varepsilon^S \dot{\mathbf{X}} + \sum_{\alpha=1}^A \rho^\alpha \varepsilon^\alpha (\dot{\mathbf{X}}^\alpha - \dot{\mathbf{X}}) + \\ &\quad + \mathbf{P}^{ST} \mathbf{F}^S \dot{\mathbf{X}} - \sum_{\alpha=1}^A \mathbf{P}^{\alpha T} \mathbf{F}^S (\dot{\mathbf{X}}^\alpha - \dot{\mathbf{X}}),\end{aligned}\tag{125}$$

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

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

$$\frac{\partial}{\partial t} \rho \left(\varepsilon + \frac{1}{2} \dot{x}^2 \right) + \text{Div} \left\{ \rho \left(\varepsilon + \frac{1}{2} \dot{x}^2 \right) \dot{\mathbf{X}} + \mathbf{Q} - \mathbf{P}^T \dot{\mathbf{x}} \right\} = \rho \mathbf{b} \cdot \dot{\mathbf{x}} + \rho r,\tag{126}$$

where

$$\begin{aligned}\rho \mathbf{b} &:= \rho^S \mathbf{b}^S + \sum_{\alpha=1}^A \rho^\alpha \mathbf{b}^\alpha, \\ \rho r &:= \rho^S r^S + \sum_{\alpha=1}^A \rho^\alpha r^\alpha - \rho^S \mathbf{b}^S \cdot \mathbf{F}^S \dot{\mathbf{X}} + \sum_{\alpha=1}^A \rho^\alpha \mathbf{b}^\alpha \cdot \mathbf{F}^S (\dot{\mathbf{X}}^\alpha - \dot{\mathbf{X}}),\end{aligned}\tag{127}$$

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

We skip the presentation of the energy condition on a singular surface because it shall not be used in these notes.

In the Lagrangian description and with the choice of fields (111) we have at disposal the following integrability condition

$$\frac{\partial \mathbf{F}^S}{\partial t} = \text{Grad } \dot{\mathbf{x}}^S.\tag{128}$$

This condition yields the existence of the function of motion (112). By the choice (111) of unknown fields this relation plays the role of the field equation for the deformation gradient \mathbf{F}^S .

It is useful to write equation (128) in the following weaker form

$$\frac{d}{dt} \int_{\mathcal{P}^S} \mathbf{F}^S dV = \oint_{\partial \mathcal{P}^S} \dot{\mathbf{x}}^S \otimes \mathbf{N} dV, \quad (129)$$

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

$$U [[\mathbf{F}^S]] = - [[\dot{\mathbf{x}}^S]] \otimes \mathbf{N}. \quad (130)$$

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

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

In order to turn over mass balance equations (118), momentum balance equations (120), energy balance equation (126) and compatibility condition (128) into field equations for fields (111) we need constitutive relations for partial stress tensors, momentum sources, the bulk internal energy and the bulk heat flux. If we had these relations we would have $14(A+1)$ equations. Consequently we would be missing one equation. This is connected with the fact that the porosity n is the additional microstructural variable and this requires an additional equation. We proceed to formulate this equation.

We have seen in Section 5 that changes of porosity may be described by a balance equation (104). This was the consequence of incompressibility of components. If the components are compressible we are missing this equation. Compressibility of components is an important feature in the wave analysis and many other problems of practical bearing and linear models (e.g. Biot's model which we present further in these notes) yield in such cases a relation for porosity which does not coincide with this derived for incompressible materials. In addition the porosity equation following from the mass conservation law does not contain a source. Such a source would describe a spontaneous relaxation of porosity. We know from experience with other microstructural variables that this is an important property yielding evolution equations for such variables. All these arguments can be made more precise if we derive an equation for porosity from a semimacroscopic model. This was done by a multiscaling technique in the work [57].

Bearing the above remarks in mind we introduce in regular points the *balance equation of porosity* in the following general form

$$\frac{\partial \Delta_n}{\partial t} + \text{Div } \mathbf{J} = \hat{n}, \quad \Delta_n = n - n_E, \quad (131)$$

where Δ_n is the deviation of porosity from the equilibrium value, the latter together with the flux of porosity \mathbf{J} and the source of porosity \hat{n} must be given by constitutive relations.

We expect that n tends to an equilibrium under constant external conditions. The equilibrium value of porosity n_E satisfies the equation (131) with the flux and source equal to zero. The latter as we show later follow indeed from the second law of thermodynamics.

Making an assumption that sources of porosity do not carry surface singularities we can write the following compatibility condition for porosity on such surfaces

$$U [[\Delta_n]] - [[\mathbf{J}]] \cdot \mathbf{N} = 0, \quad (132)$$

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

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

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

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

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

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

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

In order to construct field equations for the fields \mathbf{u} listed in relation (111) we have to solve the *closure problem*, i.e. we have to add to balance equations of the Table 1 constitutive relations. We shall do so for some important particular cases. As the first closure we select the simplest possible one which yields a possibility of exploiting the second law of thermodynamics in a way typical for the rational extended thermodynamics. The other cases shall be investigated by means of the classical approach to the exploitation of the second law of thermodynamics.

In the case of the extended thermodynamics method we proceed as follows.

Let us define the following vectors

$$\begin{aligned}
\mathbf{F}_0 &:= \left\{ \rho^S, \rho^\alpha, \rho^S \dot{\mathbf{x}}^S, \rho^\alpha \dot{\mathbf{x}}^\alpha, \rho \left(\varepsilon + \frac{1}{2} \dot{x}^2 \right), \mathbf{F}^S, \Delta_n \right\} \in \mathfrak{R}^{4A+15}, \\
\mathbf{F}_K &:= \left\{ 0, \rho^\alpha \dot{\mathbf{X}}^\alpha \cdot \mathbf{G}_K, -\mathbf{P}^S \mathbf{G}_K, \left(\rho^\alpha \dot{\mathbf{x}}^\alpha \otimes \dot{\mathbf{X}}^\alpha - \mathbf{P}^\alpha \right) \mathbf{G}_K, \right. \\
&\quad \left. \left(\rho \left(\varepsilon + \frac{1}{2} \dot{x}^2 \right) \dot{\mathbf{X}} + \mathbf{Q} - \mathbf{P}^T \dot{\mathbf{x}} \right) \cdot \mathbf{G}_K, -\dot{\mathbf{x}}^S \otimes \mathbf{G}_K, \mathbf{J} \cdot \mathbf{G}_K \right\} \in \mathfrak{R}^{4A+15}, \\
&\quad K = 1, 2, 3, \\
\mathbf{f} &:= \{ \hat{\rho}^S, \hat{\rho}^\alpha, \hat{\mathbf{p}}^S, \hat{\mathbf{p}}^\alpha, 0, \mathbf{0}, \hat{n} \} \in \mathfrak{R}^{4A+15}, \\
\mathbf{f}_{ext} &:= \{ 0, 0, \rho^S \mathbf{b}^S, \rho^\alpha \mathbf{b}^\alpha, \rho \mathbf{b} \cdot \dot{\mathbf{x}} + \rho r, \mathbf{0}, 0 \} \in \mathfrak{R}^{4A+15},
\end{aligned} \tag{133}$$

where \mathbf{G}_K denote *unit basis vectors* of Lagrangian coordinates. Then the balance equations can be written in the following compact form

$$\frac{\partial \mathbf{F}_0}{\partial t} + \frac{\partial \mathbf{F}_K}{\partial X^K} = \mathbf{f} + \mathbf{f}_{ext}, \tag{134}$$

where $\{X^K\}_{K=1,2,3}$ denote Lagrangian coordinates. For convenience we have chosen a Cartesian coordinate system.

In procedures of *extended thermodynamics* [35] it is assumed that the vectors defined by (133) are sufficiently smooth functions of the vector \mathbf{u} of unknown fields. Then the closure assumption has the form

$$\mathbf{F}_0 = \mathbf{F}_0(\mathbf{u}), \quad \mathbf{F}_K = \mathbf{F}_K(\mathbf{u}), \quad \mathbf{f} = \mathbf{f}(\mathbf{u}). \tag{135}$$

In the case under considerations we obtain the model of *poroelastic materials* without heat conduction. In order to incorporate the heat conduction we would have to introduce either an equation for the heat flux or a dependence on $\text{Grad } T$ as a constitutive variable. Similarly we would have to extend the model if we wanted to describe viscous or plastic effects - we would have to add equations for partial stresses or a dependence on gradients of partial velocities. Further we present models in which some aspects of such extensions are indeed discussed within a classical approach to the problem of thermodynamical admissibility.

Let us mention in passing that the structure of constitutive relations (135) is one of the most characteristic features of extended thermodynamics. Namely the constitutive variables are fields themselves but not their derivatives as it is always the case in ordinary nonequilibrium thermodynamics.

In order to expose the structure characteristic for extended thermodynamics we consider a simpler case of the closure in the form (135) under the assumption that processes are *isothermal*. This means that we leave out the temperature in the definition (111) of \mathbf{u} and denote it then \mathbf{u}_{is} as well as we ignore the energy balance equation.

The set of equations (135) for \mathbf{u}_{is} without energy balance has thermodynamically the same structure as the corresponding set of extended thermodynamics. For this reason we can apply the same principles connected with the **thermodynamical admissibility**. They can be formulated as follows:

- *entropy inequality*: there exist a nontrivial entropy function h_0 and a flux $\mathbf{H} = H_K \mathbf{G}_K$ such that for each thermodynamical process (i.e. for each solution of field equations) the following inequality is satisfied

$$\frac{\partial h_0}{\partial t} + \text{Div } \mathbf{H} \geq 0, \quad h_0 = h_0(\mathbf{u}_{is}) \in \mathfrak{R}, \quad \mathbf{H} = \mathbf{H}(\mathbf{u}_{is}) \in \mathfrak{R}^3, \quad (136)$$

- *convexity and causality*: the entropy function $h_0 = h_0(\mathbf{u}_{is})$ is concave, i.e.

$$\forall \mathbf{v} \in \mathfrak{R}^{14(A+1)}, \mathbf{v} \neq \mathbf{0} : \quad \frac{\partial^2 h_0}{\partial \mathbf{u}_{is} \partial \mathbf{u}_{is}} \cdot (\mathbf{v} \otimes \mathbf{v}) < 0, \quad (137)$$

- *principle of relativity (Galilean invariance of field equations)*.

The last principle yields a decomposition of all quantities of the model into two parts: a convective part which depends explicitly on the absolute velocity fields and a nonconvective part which does not depend on absolute velocities at all. This principle is satisfied identically in the case of Lagrangian description because we deal solely with relative velocities.

Entropy inequality (136) is exploited by means of Lagrange multipliers which eliminate the limitation of this inequality to thermodynamical processes. According to this procedure requirement (136) is equivalent to the following inequality for *all fields*, and not only for solutions of field equations

$$\forall \mathbf{u}_{is} \in \mathfrak{R}^{14(A+1)} : \quad \frac{\partial h_0}{\partial t} + \frac{\partial H_K}{\partial X^K} - \mathbf{\Lambda} \cdot \left(\frac{\partial \tilde{F}_0}{\partial t} + \frac{\partial \tilde{F}_K}{\partial X^K} - \tilde{f} \right) \geq 0, \quad \mathbf{\Lambda} \in \mathfrak{R}^{14(A+1)},$$

$$\mathbf{H} = H_K \mathbf{G}_K, \quad (138)$$

where $\mathbf{\Lambda}$ are the Lagrange multipliers, and functions of \mathbf{u}_{is} . As mentioned above $\tilde{F}_0, \tilde{F}_K, \tilde{f}$ are truncations of functions (133) to the subspace $\mathfrak{R}^{14(A+1)}$ without the energy balance equation.

The solution of the above problem has the following form

$$dh_0 = \mathbf{\Lambda} \cdot d\tilde{\mathbf{F}}_0, \quad dH_K = d\tilde{\mathbf{F}}_K \cdot \mathbf{\Lambda} \quad \implies \quad \frac{\partial \mathbf{\Lambda}}{\partial \mathbf{u}_{is}} = \frac{\partial^2 h_0}{\partial \mathbf{u}_{is} \partial \mathbf{u}_{is}}, \quad (139)$$

i.e. according to (137), the map $\mathbf{u}_{is} \rightarrow \mathbf{\Lambda}$ is globally invertible. Hence after Legendre transformation

$$\begin{aligned} h'_0(\mathbf{\Lambda}) &= \mathbf{\Lambda} \cdot \tilde{\mathbf{F}}_0 - h_0, \quad H'_K(\mathbf{\Lambda}) = \mathbf{\Lambda} \cdot \tilde{\mathbf{F}}_K - H_K \quad \implies \\ \implies \quad \tilde{\mathbf{F}}_0 &= \frac{\partial h'_0}{\partial \mathbf{\Lambda}}, \quad \tilde{\mathbf{F}}_K = \frac{\partial H'_K}{\partial \mathbf{\Lambda}}, \quad \mathbf{\Lambda} \cdot \tilde{\mathbf{f}}(\mathbf{\Lambda}) \geq 0. \end{aligned} \quad (140)$$

Consequently, the functions $\tilde{\mathbf{F}}_0$, and $\tilde{\mathbf{F}}_K$ which determine the left-hand side of the field equations are given if the *four-potential* $(h'_0(\mathbf{\Lambda}), H'_K(\mathbf{\Lambda}))$ is known. It leaves unspecified but restricted by the *dissipation inequality* (140)₅ only the sources $\tilde{\mathbf{f}}(\mathbf{\Lambda})$ of the field equations. This is one of the most important consequences of the second law within the rational extended thermodynamics. Moreover relations (140) yield the symmetry of field equations for the unknown vector $\mathbf{\Lambda}$:

$$\frac{\partial^2 h_0}{\partial \mathbf{\Lambda} \partial \mathbf{\Lambda}} \frac{\partial \mathbf{\Lambda}}{\partial t} + \frac{\partial^2 H'_K}{\partial \mathbf{\Lambda} \partial \mathbf{\Lambda}} \frac{\partial \mathbf{\Lambda}}{\partial X^K} = \tilde{\mathbf{f}}. \quad (141)$$

Consequently under the second part of the condition of thermodynamical admissibility (i.e. nonsingularity of matrix $\frac{\partial^2 h_0}{\partial \mathbf{\Lambda} \partial \mathbf{\Lambda}}$) the system is *symmetric hyperbolic*.

It remains to invert the variables, i.e. to find the map $\mathbf{\Lambda} \rightarrow \mathbf{u}_{is}$. This is usually a very difficult technical problem. For this reason we use further a classical approach which does not require the execution of the last step.

Let us mention that the residual inequality (140)₅ defines the *dissipation*. This function vanishes in states called *the thermodynamical equilibrium states*. Consequently the necessary and sufficient conditions for the thermodynamical equilibrium within the model discussed in this Section have the form

$$\begin{aligned} \hat{\rho}^\alpha|_E &= 0 \quad \text{for } \alpha = 1, \dots, A, \\ \hat{\mathbf{p}}^\alpha|_E &= 0 \quad \text{for } \alpha = 1, \dots, A, \\ \hat{n}|_E &= 0. \end{aligned} \quad (142)$$

They follow directly from definition (133)₃ of the vector \mathbf{f} truncated to $\tilde{\mathbf{f}}$.

Some additional details concerning thermodynamical properties of such a model can be found in the article [63].

We proceed to discuss some particular models following from the above thermodynamical scheme.

7 Two-component models with constitutive relations for porosity

7.1 Fields and field equations

In this Section we investigate models of porous materials in which porosity satisfies a constitutive relation. We consider two classes of the models [66]. In the first class labeled (*I*) we assume that the real fluid in pores is incompressible. This is a weaker assumption than this of the full incompressibility discussed earlier. This assumption means that changes of the geometry of the medium are controlled by two independent processes. On the one hand the skeleton may macroscopically deform and the porosity remains constant. Only the deformation gradient \mathbf{F}^S changes. We say that the process proceeds in *undrained conditions*. On the other hand the porosity may change by the drainage and still the macroscopic geometry of the skeleton may remain unchanged: $\mathbf{F}^S = 1$. Then changes of mass density of the fluid are determined by changes of porosity alone

$$\rho_t^F = n\rho^{FR}, \quad \rho^{FR} = \text{const.} \quad (143)$$

In the second class of models labeled (*C*) we allow for arbitrary changes of mass densities ρ_t^F, ρ_t^S but the porosity is assumed to be given by a constitutive relation. In a general case this relation is assumed to be of the form $n = n(\rho_t^F/\rho_t^S)$ which is the consequence of the dimensional analysis for isotropic materials. In this section, we assume the simplest form of this relation

$$n = n_0 \frac{\rho_t^F}{\rho_0^F} \frac{\rho_0^S}{\rho_t^S}, \quad (144)$$

where ρ_t^F, ρ_t^S, n_0 denote reference constant values of partial mass densities and the porosity.

Let us note that in general the porosity n may change as well without accompanying changes of macroscopic mass densities ρ_t^F, ρ_t^S . This happens when changes of n are compensated by changes of real mass densities ρ^{FR}, ρ^{SR} in such a way that their products $n\rho^{FR}, (1-n)\rho^{SR}$ remain constant. Such changes are not controllable on the macroscopic level. They must proceed spontaneously. Consequently they yield a relaxation of porosity characteristic for microstructural variables. Relaxation properties are, of course, dissipative. They require a source term in the relation for changes of porosity and the corresponding equation has been demonstrated in the previous Section. We return to such models further in these notes.

Fields which describe mechanical processes in the model discussed in this Section are as follows

1. the reference partial mass density of the fluid component

$$\rho^F = \rho^F(\mathbf{X}, t) = \rho_t^F J^S \equiv n J^S \rho^{FR}, \quad J^S := \det \mathbf{F}^S, \quad \mathbf{X} \in \mathcal{B}_0, \quad (145)$$

2. the field of partial velocity of the skeleton $\dot{\mathbf{x}}^S(\mathbf{X}, t)$ on the macroscopic level of description,
3. the field of partial velocity of the fluid $\dot{\mathbf{x}}^F(\mathbf{X}, t)$ on the macroscopic level of description,

4. the macroscopic deformation gradient of the skeleton $\mathbf{F}^S(\mathbf{X}, t)$.

By means of the velocity fields one can define the macroscopic filter velocity $\mathbf{w}(\mathbf{X}, t)$, and its corresponding Lagrangian image $\dot{\mathbf{X}}^F(\mathbf{X}, t)$ appearing in balance equations

$$\mathbf{w} := \dot{\mathbf{x}}^F - \dot{\mathbf{x}}^S, \quad \dot{\mathbf{X}}^F := \mathbf{F}^{S-1} \mathbf{w}. \quad (146)$$

The reference partial mass density of the skeleton $\rho^S \equiv \rho_0^S$ does not appear among those fields because it is constant in time if we assume that there is no mass exchange between components. Its current value is given by the relation

$$\rho_t^S = \rho_0^S J^{S-1}, \quad (147)$$

which satisfies identically the partial mass conservation law in Eulerian description.

Summing up we can write the following relations for the porosity in the two above classes of the models

$$\begin{aligned} (I)\text{-models} \quad & : \quad n = J^{S-1} \frac{\rho^F}{\rho^{FR}}, \quad \rho^{FR} = \text{const.}, \\ (C)\text{-models} \quad & : \quad n = \frac{\rho^F}{\rho_0^{FR}}, \quad \rho_0^{FR} = \frac{\rho_0^F}{n_0} = \text{const.} \end{aligned} \quad (148)$$

The fields must fulfil the following balance equations in Lagrangian description

1. mass conservation of the fluid component

$$\frac{\partial \rho^F}{\partial t} + \text{Div} \left(\rho^F \dot{\mathbf{X}}^F \right) = 0, \quad (149)$$

2. momentum balance for the skeleton

$$\rho^S \frac{\partial \dot{\mathbf{x}}^S}{\partial t} = \text{Div} \mathbf{P}^S + \hat{\mathbf{p}}, \quad (150)$$

3. momentum balance for the fluid

$$\rho^F \left(\frac{\partial \dot{\mathbf{x}}^F}{\partial t} + \dot{\mathbf{X}}^F \cdot \text{Grad} \dot{\mathbf{x}}^F \right) = \text{Div} \mathbf{P}^F - \hat{\mathbf{p}}. \quad (151)$$

In addition the deformation gradient \mathbf{F}^S must fulfil *integrability conditions* yielding the existence of the field of motion of the skeleton. They consist of two parts.

4. Kinematic compatibility condition relates the time derivative and the gradient of velocity

$$\frac{\partial \mathbf{F}^S}{\partial t} = \text{Grad} \dot{\mathbf{x}}^S. \quad (152)$$

The second part – a geometrical compatibility condition is a symmetry relation

$$\text{Grad } \mathbf{F}^S = (\text{Grad } \mathbf{F}^S)^{\text{23}^T}, \quad (153)$$

or, in Cartesian coordinates

$$\frac{\partial F_{kK}^S}{\partial X^L} = \frac{\partial F_{kL}^S}{\partial X^K}, \quad (154)$$

where the small index refers to Eulerian coordinates, and the capital index to Lagrangian coordinates.

Obviously, all operators Grad, Div, $\frac{\partial}{\partial X^K}$ refer to Lagrangian variables.

As we have mentioned conditions (152), (153) yield the existence of the field of motion of skeleton, say $\chi^S(\mathbf{X}, t)$, whose derivatives give the deformation gradient and the partial velocity, vis.

$$\mathbf{F}^S = \text{Grad } \chi^S, \quad \dot{\mathbf{x}}^S = \frac{\partial \chi^S}{\partial t}. \quad (155)$$

Momentum balance equations contain partial Piola-Kirchhoff stresses $\mathbf{P}^S, \mathbf{P}^F$ which are related to the usual Cauchy stresses by the following transformation rules

$$\mathbf{T}^S = J^{S-1} \mathbf{P}^S \mathbf{F}^{ST}, \quad \mathbf{T}^F = J^{S-1} \mathbf{P}^F \mathbf{F}^{ST}. \quad (156)$$

Momentum equations contain as well the source $\hat{\mathbf{p}}$ which is the diffusion force.

We have to perform a closure in order to obtain field equations from the above balance relations. For poroelastic materials we consider further two models following from two choices of constitutive variables. Namely we choose either

$$\mathcal{C}^{(1)} = \left\{ \rho^F, \mathbf{F}^S, \dot{\mathbf{X}}^F \right\}, \quad (157)$$

or

$$\mathcal{C}^{(2)} = \left\{ \rho^F, \mathbf{F}^S, \dot{\mathbf{X}}^F, \text{Grad } n \right\}. \quad (158)$$

The porosity n does not appear among these variables because it is either given by the relation (148)₁ or by the relation (148)₂. Consequently it can be eliminated from the set of independent constitutive variables.

The following functions must be given in terms of constitutive relations

$$\mathcal{F} = \left\{ \mathbf{P}^S, \mathbf{P}^F, \hat{\mathbf{p}}, \psi^S, \psi^F \right\}, \quad (159)$$

where ψ^S, ψ^F denote partial Helmholtz free energies appearing further in the second law of thermodynamics.

For reasons of material objectivity we should choose not only the *relative* velocity as the variable but also one of the *objective measures* of deformation. We shall do so further in this note. However the exploitation of the second law of thermodynamics is easier if we impose the objectivity after the exploitation of the entropy inequality.

For any of the choices of constitutive variables constitutive relations are assumed to have the form of the relation

$$\mathcal{F} = \mathcal{F}(\mathcal{C}^{(\alpha)}), \quad \alpha = 1, 2, \quad (160)$$

which is sufficiently smooth for all operations which we perform in the sequel.

Let us make two methodological remarks.

Our main interest in comparison with Biot's model as well as in the analysis of acoustic waves is limited to linear models. Consequently the above presented nonlinear models are an overkill. We do so on purpose because the exploitation of the second law of thermodynamics for a model with linear constitutive laws cannot be made consistent with explicit nonlinear contributions to field equations. This yields serious flaws of the thermodynamical analysis known in all nonlinear field theories.

Secondly we should point out that the restriction to incompressible real fluids in the class (I) of models **does not lead to any constraints**. This may be simply interpreted as a change of variables: changes of the partial mass density of the fluid are replaced by corresponding changes of the porosity. There is no reaction force on such a "constraint". This is different from the cases which were considered previously (e.g. Section 5). In those cases the model possesses an additional equation for porosity which, in turn, is considered to be a real microstructural variable with spontaneous relaxation properties. In such models the incompressibility assumption yields the existence of the reaction pressure, and it requires a special structure of constitutive relations.

Let us mention in passing that the above change of variables may lead to some mathematical problems due to the restriction $0 < n < 1$. In a linear model changes of porosity with respect to its initial value n_0 are small. The choice of a real value of n_0 , say between 0.1 and 0.6, guarantees that this restriction is indeed fulfilled. In nonlinear models we have to take care of this constraint. If thermodynamic restrictions are derived by means of the partial mass density, which we do in this Section, such a restriction does not appear.

7.2 Thermodynamic admissibility

7.2.1 Second law of thermodynamics

We present here solely the second law of thermodynamics for two-component systems for which the temperature is constant. If this is the case it may be formulated as follows (e.g. [66]). For any solution of field equations (i.e. for any *thermodynamical process*) the following inequality

$$\begin{aligned} & \rho^S \frac{\partial \psi^S}{\partial t} + \rho^F \left(\frac{\partial \psi^F}{\partial t} + \dot{\mathbf{X}}^F \cdot \text{Grad } \psi^F \right) - \\ & - \mathbf{P}^S \cdot \frac{\partial \mathbf{F}^S}{\partial t} - \mathbf{P}^F \cdot \text{Grad } \dot{\mathbf{X}}^F - \hat{\mathbf{p}} \cdot \mathbf{w} \leq 0, \end{aligned} \quad (161)$$

must be satisfied identically.

The main technical problem by the exploitation of this inequality is the limitation to solutions of field equations. This can be eliminated by means of Lagrange multipliers introduced to thermodynamics by I-Shih Liu (e.g. [56]). Namely it can be shown that the following inequality

$$\rho^S \frac{\partial \psi^S}{\partial t} + \rho^F \left(\frac{\partial \psi^F}{\partial t} + \dot{\mathbf{X}}^F \cdot \text{Grad } \psi^F \right) - \mathbf{P}^S \cdot \frac{\partial \mathbf{F}^S}{\partial t} - \mathbf{P}^F \cdot \text{Grad } \dot{\mathbf{X}}^F - \hat{\mathbf{p}} \cdot \mathbf{w} -$$

$$\begin{aligned}
& -\Lambda^n \left\{ \frac{\partial \rho^F}{\partial t} + \text{Div} \left(\rho^F \dot{\mathbf{X}}^F \right) \right\} - \Lambda^F \cdot \left\{ \frac{\partial \mathbf{F}^S}{\partial t} - \text{Grad} \dot{\mathbf{x}}^S \right\} - \\
& -\Lambda^{vS} \cdot \left\{ \rho^S \frac{\partial \dot{\mathbf{x}}^S}{\partial t} - \text{Div} \mathbf{P}^S - \hat{\mathbf{p}} \right\} - \\
& -\Lambda^{vF} \cdot \left\{ \rho^F \left(\frac{\partial \dot{\mathbf{x}}^F}{\partial t} + \dot{\mathbf{X}}^F \cdot \text{Grad} \dot{\mathbf{x}}^F \right) - \text{Div} \mathbf{P}^F + \hat{\mathbf{p}} \right\} \leq 0,
\end{aligned} \tag{162}$$

must hold for any fields and not only for solutions of field equations. The multipliers $\Lambda^n, \Lambda^F, \Lambda^{vS}, \Lambda^{vF}$ are functions of constitutive variables $\mathcal{C}^{(\alpha)}$ for α either equal to 1 or to 2. We proceed to discuss the consequences of the above condition for these two different models.

7.2.2 $\mathcal{C}^{(1)}$ -models

We consider the model with constitutive variables given by the relation (157). It is not necessary to distinguish between (*I*)-models and (*C*)-models because the only difference appears in the final results due to the substitution of either (148)₁ or (148)₂.

It is easy to check that the chain rule of differentiation in the inequality (162) yields the linearity of this inequality with respect to the following derivatives

$$\left\{ \frac{\partial \rho^F}{\partial t}, \frac{\partial \mathbf{F}^S}{\partial t}, \frac{\partial \dot{\mathbf{x}}^S}{\partial t}, \frac{\partial \dot{\mathbf{x}}^F}{\partial t} \right\}, \tag{163}$$

as well as

$$\{ \text{Grad} \rho^F, \text{Grad} \mathbf{F}^S, \text{Grad} \dot{\mathbf{x}}^S, \text{Grad} \dot{\mathbf{x}}^F \}. \tag{164}$$

Consequently, as the inequality must hold for **all fields**, the coefficients of these derivatives have to vanish. We obtain from the contributions of time derivatives (163) the following relations

$$\begin{aligned}
\Lambda^n &= \rho^S \frac{\partial \psi^S}{\partial \rho^F} + \rho^F \frac{\partial \psi^F}{\partial \rho^F}, \\
\mathbf{P}^S + \Lambda^F &= \rho^S \frac{\partial \psi^S}{\partial \mathbf{F}^S} + \rho^F \frac{\partial \psi^F}{\partial \mathbf{F}^S} - \rho^S \left(\mathbf{F}^{S-T} \frac{\partial \psi^S}{\partial \dot{\mathbf{X}}^F} \right) \otimes \dot{\mathbf{X}}^F - \rho^F \left(\mathbf{F}^{S-T} \frac{\partial \psi^F}{\partial \dot{\mathbf{X}}^F} \right) \otimes \dot{\mathbf{X}}^F, \\
\rho^S \Lambda^{vS} &= -\rho^F \Lambda^{vF} = -\rho^S \frac{\partial \psi^S}{\partial \dot{\mathbf{X}}^F} - \rho^F \frac{\partial \psi^F}{\partial \dot{\mathbf{X}}^F}.
\end{aligned} \tag{165}$$

On the other hand the coefficients of spatial derivatives (164) lead to the following identities

$$\begin{aligned}
& \left(\rho^F \frac{\partial \psi^F}{\partial \rho^F} - \Lambda^n \right) \dot{\mathbf{X}}^F + \frac{\partial \mathbf{P}^{ST}}{\partial \rho^F} \Lambda^{vS} + \frac{\partial \mathbf{P}^{FT}}{\partial \rho^F} \Lambda^{vF} = 0, \\
& \text{sym}^{23} \left(\frac{\partial \psi^F}{\partial \mathbf{F}^S} + \Lambda^n \mathbf{F}^{S-T} \right) \otimes \dot{\mathbf{X}}^F = 0,
\end{aligned}$$

$$\mathbf{\Lambda}^F = \mathbf{P}^F = -\rho^F \mathbf{\Lambda}^n \mathbf{F}^{S-T}. \quad (166)$$

It remains the residual inequality

$$\hat{\mathbf{p}} \cdot \mathbf{w} \geq 0, \quad (167)$$

which defines the *dissipation density* of the system.

For technical reasons we make the following simplifying assumption

$$\frac{\partial \psi^S}{\partial \dot{\mathbf{X}}^F} = \frac{\partial \psi^F}{\partial \dot{\mathbf{X}}^F} = 0. \quad (168)$$

We consider further the model in which this assumption is not being made. It has consequences on nonlinear contributions of diffusion velocity.

Combination of relations (165)₁ and (166)₁ yields now

$$\mathbf{\Lambda}^n = \rho^F \frac{\partial \psi^F}{\partial \rho^F}, \quad \frac{\partial \psi^S}{\partial \rho^F} = 0. \quad (169)$$

The second part of this relation has the most important bearing on the structure of interactions described by the model. Namely the partial free energy of the skeleton does not react on changes of the porosity. We see in a moment what is the reaction of partial stresses on this property. Such a conclusion would be impossible if we performed the exploitation of the second law for a linear model.

Relation (166)₂ leads after easy calculations to the relation

$$\frac{\partial \psi^F}{\partial \mathbf{F}^S} = -\mathbf{\Lambda}^n \mathbf{F}^{S-T}. \quad (170)$$

Hence relations (165)₂ and (166)₂ yield the following relations for partial Piola-Kirchhoff stresses

$$\mathbf{P}^S = \rho^S \frac{\partial \psi^S}{\partial \mathbf{F}^S}, \quad \mathbf{P}^F = -\rho^{F2} \frac{\partial \psi^F}{\partial \rho^F} \mathbf{F}^{S-T},$$

or, after the transformation to partial Cauchy stresses, described by (156),

$$\mathbf{T}^S = \rho_t^S \frac{\partial \psi^S}{\partial \mathbf{F}^S} \mathbf{F}^{ST}, \quad \mathbf{T}^F = -p^F \mathbf{1}, \quad p^F := \rho_t^{F2} \frac{\partial \psi^F}{\partial \rho_t^F}. \quad (171)$$

These are classical thermodynamical relations for elastic materials, and ideal fluids, respectively. The most important property of these relations is the fact that identities (169)₂ and (170) yield

$$\mathbf{T}^S = \mathbf{T}^S(\mathbf{F}^S), \quad p^F = p^F(\rho_t^F). \quad (172)$$

The latter requires an assumption on isotropy and it shall be proven in the next Subsection.

Consequently, we obtain an analogon of the simple mixture model which we have considered for mixtures of fluids. It means that one **cannot obtain Biot's model** by linearization of the above model. Couplings between partial stresses which are appearing in the original Biot model with the material constant Q would have to violate the second

law of thermodynamics. This property seems to be common for all multicomponent models of poroelastic materials which do not contain higher gradients among constitutive variables.

Obviously the model contains coupling due to the relative motion of components and described by the source $\hat{\mathbf{p}}$. For this reason solutions of boundary – initial value problems and consequently local values of partial stresses follow from the **coupled** field equations.

We should also mention that the similarity of the relation for p^F for incompressible real fluids ((*I*)-models) to the relation for compressible fluids ((*C*)-models) is misleading. This relation has an entirely different physical interpretation. For compressible fluids the relation (172)₂ yields the following *linear form* of the constitutive relation for the partial pressure

$$p^F = p_0^F + \kappa (\rho^F - \rho_0^F), \quad (173)$$

where p_0^F is the reference pressure and ρ_0^F – the corresponding reference partial mass density. In such a case the compressibility coefficient κ describes elastic properties of the fluid. Simultaneously its square root specifies the speed of the longitudinal wave in the fluid. This is not the case for the model with the incompressibility assumption. As the real fluid in this case is incompressible it has no elastic properties. Consequently the relation for p^F describes its dependence on changes of porosity which are due to microscopical morphological changes of the skeleton such as a redistribution of grains. Hence acoustic properties related to such a constitutive relation for the pressure cannot be extracted from microscopic properties of the real fluid component.

Incidentally such a model supports views advocated by W. G. Gray (e.g. see: [24]) that macroscopic constitutive relations of components in the macroscopic model cannot be directly related to constitutive properties of real components, and even less they can be derived by any averaging procedure for a single real microscopic component. Macroscopic constitutive properties reflect for each component microscopic properties of both real components as well as microscopic interactions between them.

In the next Subsection we consider a higher gradient model which allows for interactions in constitutive relations for partial stresses.

7.2.3 $\mathcal{C}^{(2)}$ –models

We proceed to consider the model based on constitutive variables (158). However we limit the attention to the simplest case in which the model is *linear* with respect to the gradient of porosity. In such a case it may appear solely in the constitutive relation for the source $\hat{\mathbf{p}}$ because this is the only vectorial constitutive function. We simplify the model even further and assume linearity of the source with respect to both filter velocity \mathbf{w} and $\text{grad } n$. Consequently

$$\hat{\mathbf{p}} = \pi \mathbf{w} - N \text{grad } n, \quad (174)$$

where material parameters π and N may still depend on ρ^F and \mathbf{F}^S . We have left out a possible nonlinear contribution proportional to the vector product $\mathbf{w} \times \text{grad } n$ which would appear in a general nonlinear isotropic model. In contrast to linear contributions such a term would be nondissipative. The minus sign in (174) is related to the property of incompressible models in which N coincides with the pore pressure. In general it may

not be the case. This parameter seems to be always positive. However such a property does not follow from the second law of thermodynamics.

We assume also the relation (168) to hold.

Bearing the relation (148) in mind we obtain the following contribution of the source to the inequality (162)

$$\begin{aligned}
(I)\text{-models} & : \quad \hat{\mathbf{p}} \cdot \mathbf{w} = \pi \mathbf{w} \cdot \mathbf{w} - N \frac{1}{\rho^{FR} J^S} \left\{ \text{Grad } \rho^F - \rho^F \mathbf{F}^{ST} \text{Div } \mathbf{F}^{S-1} \right\} \cdot \dot{\mathbf{X}}^F, \\
(C)\text{-models} & : \quad \hat{\mathbf{p}} \cdot \mathbf{w} = \pi \mathbf{w} \cdot \mathbf{w} - N \frac{1}{\rho_0^{FR}} \text{Grad } \rho^F \cdot \dot{\mathbf{X}}^F, \quad \mathbf{w} \equiv \mathbf{F}^S \dot{\mathbf{X}}^S. \quad (175)
\end{aligned}$$

Contributions appearing with the parameter N in these relations change the identities of the previous Subsection following from coefficients of spatial derivatives. Namely relations (166)₁ and (166)₂ will be influenced. We collect all these results of the second law of thermodynamics in the juxtaposition.

Table 1

(I)-models	(C)-models
$\Lambda^n = \rho^S \frac{\partial \psi^S}{\partial \rho^F} + \rho^F \frac{\partial \psi^F}{\partial \rho^F},$	$\Lambda^n = \rho^S \frac{\partial \psi^S}{\partial \rho^F} + \rho^F \frac{\partial \psi^F}{\partial \rho^F},$
$\mathbf{P}^S = \rho^S \frac{\partial \psi^S}{\partial \mathbf{F}^S} + \rho^F \frac{\partial \psi^F}{\partial \mathbf{F}^S} - \mathbf{P}^F,$	$\mathbf{P}^S = \rho^S \frac{\partial \psi^S}{\partial \mathbf{F}^S} + \rho^F \frac{\partial \psi^F}{\partial \mathbf{F}^S} - \mathbf{P}^F,$
$\mathbf{P}^F = -\rho^F \Lambda^n \mathbf{F}^{S-T},$	$\mathbf{P}^F = -\rho^F \Lambda^n \mathbf{F}^{S-T},$
$\rho^S \frac{\partial \psi^S}{\partial \rho^F} - \frac{N}{\rho^{FR}} J^{S-1} = 0, \quad \rho^{FR} = \text{const.}$	$\rho^S \frac{\partial \psi^S}{\partial \rho^F} - \frac{N}{\rho_0^{FR}} = 0,$
$\frac{\partial \psi^F}{\partial \mathbf{F}^S} + \rho^F \frac{\partial \psi^F}{\partial \rho^F} \mathbf{F}^{S-T} = 0,$	$\frac{\partial \psi^F}{\partial \mathbf{F}^S} + \left(\rho^F \frac{\partial \psi^F}{\partial \rho^F} + \frac{N}{\rho_0^{FR}} \right) \mathbf{F}^{S-T} = 0.$

After easy manipulations we obtain the following relations for the partial Piola-Kirchhoff stresses in both classes of models

$$\begin{aligned}
(I)\text{-models} & : \quad \mathbf{P}^S = \rho^S \frac{\partial \psi^S}{\partial \mathbf{F}^S} + n N \mathbf{F}^{S-T}, \\
(C)\text{-models} & : \quad \mathbf{P}^S = \rho^S \frac{\partial \psi^S}{\partial \mathbf{F}^S},
\end{aligned} \quad (176)$$

$$(I)\text{-models \& } (C)\text{-models: } \mathbf{P}^F = - \left(\rho^{F2} \frac{\partial \psi^F}{\partial \rho^F} + nN \right) \mathbf{F}^{S-T}, \quad (177)$$

as well as the following identities for partial free energy functions

$$\begin{aligned} (I)\text{-models} & : \quad \frac{\partial \psi^F}{\partial \mathbf{F}^S} = -\rho^F \frac{\partial \psi^F}{\partial \rho^F} \mathbf{F}^{S-T}, \quad \rho^S \frac{\partial \psi^S}{\partial \rho^F} = \frac{N}{\rho^{FR} J^S}, \\ (C)\text{-models} & : \quad \frac{\partial \psi^F}{\partial \mathbf{F}^S} = - \left(\rho^F \frac{\partial \psi^F}{\partial \rho^F} + \frac{N}{\rho_0^{FR}} \right) \mathbf{F}^{S-T}, \quad \rho^S \frac{\partial \psi^S}{\partial \rho^F} = \frac{N}{\rho_0^{FR}}. \end{aligned} \quad (178)$$

Then for the partial Cauchy stresses follow the relations of the form

$$\begin{aligned} (I)\text{-models} & : \\ \mathbf{T}^S & = \rho^S J^{S-1} \frac{\partial \psi^S}{\partial \mathbf{F}^S} \mathbf{F}^{ST} + nN J^{S-1} \mathbf{1}, \quad \mathbf{T}^F = -p^F \mathbf{1}, \\ p^F & : = \rho^{F2} J^{S-1} \frac{\partial \psi^F}{\partial \rho^F} + nN J^{S-1}, \\ (C)\text{-models} & : \\ \mathbf{T}^S & = \rho^S J^{S-1} \frac{\partial \psi^S}{\partial \mathbf{F}^S} \mathbf{F}^{ST}, \quad \mathbf{T}^F = -p^F \mathbf{1}, \\ p^F & : = \rho^{F2} J^{S-1} \frac{\partial \psi^F}{\partial \rho^F} + nN J^{S-1}. \end{aligned} \quad (179)$$

It is seen that both models contain couplings of stresses which may lead to the Biot's constitutive relations for stresses (e.g. [12], [43]) of the linear model. We proceed to investigate this question.

In order to simplify the construction of the linear model we evaluate the above non-linear relations for isotropic materials. In such a case free energies ψ^S, ψ^F satisfying the principle of material objectivity depend on the deformation gradient \mathbf{F}^S solely through the invariants of its symmetric part. For instance we can choose the invariants of the right Cauchy – Green deformation tensor \mathbf{C}^S

$$\mathbf{C}^S := \mathbf{F}^{ST} \mathbf{F}^S, \quad I := \text{tr } \mathbf{C}^S, \quad II := \frac{1}{2} (I^2 - \text{tr } \mathbf{C}^{S2}), \quad III \equiv J^{S2} := \det \mathbf{C}^S. \quad (180)$$

Then

$$\psi^S = \psi^S(I, II, III, \rho^F), \quad \psi^F = \psi^F(I, II, III, \rho^F). \quad (181)$$

Let us exploit the identity (178)₁ under the above assumption. Bearing the following relation in mind

$$\frac{\partial \psi^F}{\partial \mathbf{F}^S} = 2\mathbf{F}^S \frac{\partial \psi^F}{\partial \mathbf{C}^S}, \quad (182)$$

we obtain

$$\begin{aligned} \frac{\partial \psi^F}{\partial \mathbf{F}^S} \mathbf{F}^{ST} & = 2 \left(\frac{\partial \psi^F}{\partial I} \mathbf{B}^S + \frac{\partial \psi^F}{\partial II} I \mathbf{B}^S - \frac{\partial \psi^F}{\partial II} \mathbf{B}^{S2} + \frac{\partial \psi^F}{\partial III} III \mathbf{1} \right), \\ \mathbf{B}^S & : = \mathbf{F}^S \mathbf{F}^{ST}, \quad III \equiv J^{S2}, \end{aligned} \quad (183)$$

where the symmetric tensor \mathbf{B}^S is called the left Cauchy-Green deformation tensor. Now we can write (178)₁ in the form

(*I*)-models :

$$\left(2III \frac{\partial \psi^F}{\partial III} + \rho^F \frac{\partial \psi^F}{\partial \rho^F}\right) \mathbf{1} + 2 \left(\frac{\partial \psi^F}{\partial I} + \frac{\partial \psi^F}{\partial II} I\right) \mathbf{B}^S - 2 \frac{\partial \psi^F}{\partial II} \mathbf{B}^{S2} = 0, \quad (184)$$

(*C*)-models :

$$\left(2III \frac{\partial \psi^F}{\partial III} + \rho^F \frac{\partial \psi^F}{\partial \rho^F} + \frac{N}{\rho_0^{FR}}\right) \mathbf{1} + 2 \left(\frac{\partial \psi^F}{\partial I} + \frac{\partial \psi^F}{\partial II} I\right) \mathbf{B}^S - 2 \frac{\partial \psi^F}{\partial II} \mathbf{B}^{S2} = 0.$$

These relations must hold for arbitrary deformations \mathbf{B}^S . Consequently, according to the corollaries of the Cayley-Hamilton theorem in the tensor analysis, coefficients of tensors $\mathbf{1}, \mathbf{B}^S, \mathbf{B}^{S2}$ have to vanish independently. Hence in both cases the free energy ψ^F must be independent of invariants I, II , and, consequently (comp. relations for N in Table 1) N must be independent of these two invariants in (*C*)-models but not necessarily in (*I*)-models. In addition we have

$$(I)\text{-models} \quad : \quad \psi^F = \psi^F(J^S, \rho^F), \quad J^S \frac{\partial \psi^F}{\partial J^S} + \rho^F \frac{\partial \psi^F}{\partial \rho^F} = 0; \quad (185)$$

$$(C)\text{-models} \quad : \quad \psi^F = \psi^F(J^S, \rho^F), \quad J^S \frac{\partial \psi^F}{\partial J^S} + \rho^F \frac{\partial \psi^F}{\partial \rho^F} = -\frac{N}{\rho_0^{FR}}, \quad (186)$$

$$N = N(J^S, \rho^F).$$

The differential equation (185)₂ for (*I*)-models can be easily solved by the method of characteristics. If we denote the variable along the characteristic by ξ then we can write this equation in the characteristic form

$$\frac{dJ^S}{d\xi} = J^S, \quad \frac{d\rho^F}{d\xi} = \rho^F, \quad \frac{d\psi^F}{d\xi} = 0. \quad (187)$$

Consequently ψ^F is constant along the characteristics, and these are labeled by the following initial values

$$\rho^F J^{S-1} = \text{const}, \quad (188)$$

which follows from (187)_{1,2}. It means that the solution of the identity (178)₁ for isotropic materials with incompressible real fluid is of the form

$$(I)\text{-models: } \psi^F = \psi^F(\rho_t^F). \quad (189)$$

The problem is more complicated for compressible materials. However we can simplify the equation (186)₂ if we change the variables in a way suggested by the above solution for the (*I*)-model. Namely we obtain

$$(C)\text{-models} \quad : \quad (\rho^F, J^S) \rightarrow (\rho_t^F, J^S) \implies \psi^F = \psi^F(\rho_t^F, J^S) \quad (190)$$

and

$$J^S \frac{\partial \psi^F}{\partial J^S} = -\frac{N}{\rho_0^{FR}} \implies \psi^F = \psi_{ideal}^F(\rho_t^F) - \frac{1}{\rho_0^{FR}} \int_1^{J^S} \frac{N(\rho_t^F, \xi)}{\xi} d\xi. \quad (191)$$

It is instructive to apply the relation (178)₂ in the formulae (179) for Cauchy stresses. For isotropic materials we obtain immediately

(*I*)-models:

$$\begin{aligned}\mathbf{T}^S &= \rho^S J^{S-1} \left\{ \left(J^S \frac{\partial \psi^S}{\partial J^S} + \rho^F \frac{\partial \psi^S}{\partial \rho^F} \right) \mathbf{1} + 2 \left(\frac{\partial \psi^S}{\partial I} + I \frac{\partial \psi^S}{\partial II} \right) \mathbf{B}^S - 2 \frac{\partial \psi^S}{\partial II} \mathbf{B}^{S2} \right\}, \\ \mathbf{T}^F &= -\rho^F J^{S-1} \left(\rho^F \frac{\partial \psi^F}{\partial \rho^F} + \rho^S \frac{\partial \psi^S}{\partial \rho^F} \right) \mathbf{1},\end{aligned}\tag{192}$$

(*C*)-models:

$$\begin{aligned}\mathbf{T}^S &= \rho^S J^{S-1} \left\{ J^S \frac{\partial \psi^S}{\partial J^S} \mathbf{1} + 2 \left(\frac{\partial \psi^S}{\partial I} + I \frac{\partial \psi^S}{\partial II} \right) \mathbf{B}^S - 2 \frac{\partial \psi^S}{\partial II} \mathbf{B}^{S2} \right\}, \\ \mathbf{T}^F &= -\rho^F J^{S-1} \left(\rho^F \frac{\partial \psi^F}{\partial \rho^F} + \rho^S \frac{\partial \psi^S}{\partial \rho^F} \right) \mathbf{1}.\end{aligned}\tag{193}$$

Let us discuss first the structure of stress relations for (*I*)-models. As indicated by (189) the first contribution to the partial stress \mathbf{T}^F cannot contain any coupling to the deformation of the skeleton. Consequently it is the derivative of the partial Helmholtz free energy ψ^S with respect to ρ_t^F which relates \mathbf{T}^F to the deformation of the skeleton. According to the relation (178)₂ for the existence of this coupling the coefficient N must be different from zero. For the symmetry required in the Biot's model it is necessary to introduce a rather complicated dependence of the partial free energy function ψ^S on the mass density ρ^F which would create a term in $\rho^S \frac{\partial \psi^S}{\partial J^S}$ canceling out the contribution $\rho^S \rho^F J^{S-1} \frac{\partial \psi^S}{\partial \rho^F}$ to the stress \mathbf{T}^S (the wrong sign!) and simultaneously produces another one introducing the coupling to the deformation of the fluid. Even though it is possible in principle such a model does not seem to be very plausible and we do not investigate it any further.

Let us mention in passing that in a particular case of the constant partial free energy ψ^F the relation (179)₂ for incompressible real fluids yields $N = \frac{p^F}{n}$ which is the pore pressure of classical models. Hence in this particular case the coefficient in the diffusion force (174) coincides with that of classical models of consolidation. This structure has been indicated in the work [51] on nonlinear sources.

The structure of stress relations for (*C*)-models is simpler. As thermodynamical requirements do not lead to any restrictions of the free energy ψ^S on ρ_t^F , and the free energy ψ^F on J^S we may produce as a particular case a desired dependence and symmetry. We shall do so for the linear model.

Concluding the above thermodynamical considerations we see that the Biot's constitutive relations for stresses can be derived from nonlinear $\mathcal{C}^{(2)}$ -models by a specific choice of partial free energies. It means that such a transition requires a higher gradient model as a background.

7.3 Linear models

Among linear models describing two-component (saturated) poroelastic materials the most frequently used is the Biot model. We quote the fundamental relations of the

classical Biot model in a chosen inertial frame of reference (e.g. [12] [43])

$$\rho_0^S \frac{\partial \mathbf{v}^S}{\partial t} = \lambda^S \operatorname{grad} \operatorname{tr} \mathbf{e}^S + 2\mu^S \operatorname{div} \mathbf{e}^S + Q \operatorname{grad} \varepsilon + \pi (\mathbf{v}^F - \mathbf{v}^S) - \rho_{12} \left(\frac{\partial \mathbf{v}^F}{\partial t} - \frac{\partial \mathbf{v}^S}{\partial t} \right), \quad (194)$$

$$\rho_0^F \frac{\partial \mathbf{v}^F}{\partial t} = \kappa \rho_0^F \operatorname{grad} \varepsilon + Q \operatorname{grad} \operatorname{tr} \mathbf{e}^S - \pi (\mathbf{v}^F - \mathbf{v}^S) + \rho_{12} \left(\frac{\partial \mathbf{v}^F}{\partial t} - \frac{\partial \mathbf{v}^S}{\partial t} \right),$$

where

$$\frac{\partial \mathbf{e}^S}{\partial t} = \operatorname{sym} \operatorname{grad} \mathbf{v}^S, \quad \frac{\partial \varepsilon}{\partial t} = \operatorname{div} \mathbf{v}^F, \quad \varepsilon := \frac{\rho_0^F - \rho_t^F}{\rho_0^F} \equiv \operatorname{tr} \mathbf{e}^S - \frac{\zeta}{n_0}, \quad (195)$$

and \mathbf{e}^S denotes the macroscopical Almansi-Hamel **deformation tensor of the skeleton**, its trace, $\operatorname{tr} \mathbf{e}^S$, is the **volume change** (small deformations!) **of the skeleton**, ε is the **volume change of the fluid** and this is related to the **increment of fluid content**, ζ , by the relation (195)₃. ρ_t^F denotes the current partial density of the fluid component. ρ_0^S, ρ_0^F are constant initial partial mass densities connected to the true mass densities ρ_0^{SR}, ρ_0^{FR} in the following way

$$\rho_0^S = (1 - n_0) \rho_0^{SR}, \quad \rho_0^F = n_0 \rho_0^{FR}, \quad (196)$$

where n_0 is the initial porosity. $\mathbf{v}^S, \mathbf{v}^F$ are **macroscopic velocities** of both components, i.e. $\mathbf{v}^F - \mathbf{v}^S$ is the seepage velocity. The material parameters $\lambda^S, \mu^S, \kappa, Q, \pi, \rho_{12}$ are constant.

The literature on Biot's model is far from being unique in relation to the notation and this creates a lot of confusion. The above material parameters are characteristic for the formulation of a two-component mixture. Usually in soil mechanics use is being made of the total bulk stress $\mathbf{T} = \mathbf{T}^S + \mathbf{T}^F$, and the fluid partial stress is related solely to the pore pressure p . Namely $\mathbf{T}^F = -n_0 p \mathbf{1}$.

For this reason the material parameters are introduced, for instance, in the following way [41]

$$\begin{aligned} K &:= \lambda^S + \frac{2}{3} \mu^S + \rho_0^F \kappa + 2Q, \quad G := \mu^S, \\ C &:= \frac{1}{n_0} (Q + \rho_0^F \kappa), \quad M := \frac{\rho_0^F \kappa}{n_0^2}. \end{aligned} \quad (197)$$

On the other hand in the standard reference book on linear acoustics of porous materials [14] the following form of the set (194) is used

$$\begin{aligned} \rho \frac{\partial \mathbf{v}^S}{\partial t} + \rho_{uw} \frac{\partial^2 \mathbf{w}}{\partial t^2} &= \operatorname{div} \mathbf{T}, \\ \mathbf{T} &= \mathbf{T}^S + \mathbf{T}^F, \quad \mathbf{T}^F = -n_0 p \mathbf{1}, \quad \frac{\partial \mathbf{w}}{\partial t} = n_0 \left(\frac{\partial \mathbf{v}^F}{\partial t} - \frac{\partial \mathbf{v}^S}{\partial t} \right), \\ \mathbf{T} &= \lambda_f \operatorname{tr} \mathbf{e}^S \mathbf{1} + 2\mu \mathbf{e}^S - \beta M \zeta \mathbf{1}, \\ \rho_{uw} \frac{\partial \mathbf{v}^F}{\partial t} + \rho_w \frac{\partial \mathbf{w}}{\partial t} &= -\operatorname{grad} p - \frac{1}{\mathcal{K}} \mathbf{w}, \\ p &= M (-\beta \operatorname{tr} \mathbf{e}^S + \zeta), \end{aligned} \quad (198)$$

with the following relations among parameters

$$\begin{aligned}\rho &= \rho_0^S + \rho_0^F, \quad \rho_{uw} = \rho_0^{FR}, \quad \rho_w = \frac{1}{n_0^2} (\rho_0^F - \rho_{12}), \\ \lambda_f &= \lambda^S + \kappa \rho_0^F + 2Q, \quad \mu = \mu^S, \quad \beta M = \frac{1}{n_0} (Q + \kappa \rho_0^F), \quad \frac{1}{\mathcal{K}} = \frac{\pi}{n_0^2}.\end{aligned}\tag{199}$$

Still another set of parameters is used by Allard [9], where $\rho_{12} = -\rho_a$, $\rho_0^{FR} = \rho_0$, $\rho_0^S = \rho_1$, etc.

Let us return to the set (194). The parameter ρ_{12} describing the contribution of the relative acceleration is usually related to the **tortuosity** of the porous material. For example, in the works [10], [27] the following approximate relation between this parameter, the porosity n_0 , and the tortuosity parameter $a \in [1, \infty)$, is proposed

$$\rho_{12} = \rho_0^F (1 - a), \quad a = \frac{1}{2} \left(\frac{1}{n_0} + 1 \right).\tag{200}$$

We return to the problem of the contribution of relative accelerations described by the parameter ρ_{12} in the next Section of these notes.

In order to compare the relations derived in the previous Subsection with Biot's relations we have to linearize the model. The Almansi-Hamel deformation measure \mathbf{e}^S used in the Biot model is given by the relation

$$\mathbf{e}^S := \frac{1}{2} (\mathbf{1} - \mathbf{B}^{S-1}).\tag{201}$$

The linearity follows from the assumption that deformations of the skeleton are small, and that changes of porosity are small

$$\begin{aligned}\max \{ |\lambda^{(\alpha)}| \}_{\alpha=1,2,3} &\ll 1, \quad \det (\mathbf{e}^S - \lambda^{(\alpha)} \mathbf{1}) = 0, \\ |\varsigma| &\ll 1, \quad \varsigma := \frac{n - n_0}{n_0},\end{aligned}\tag{202}$$

where $\lambda^{(\alpha)}$ are eigenvalues of \mathbf{e}^S , and they are called principal deformations while n_0 denotes the reference constant value of porosity.

We construct the linear version of the (C)-model. In this model, also in its fully nonlinear version, the porosity is related to the mass density by the relation (151)₂, i.e.

$$n = \frac{\rho_t^F J^S}{\rho_0^{FR}}.\tag{203}$$

The variable ς can be now coupled to changes of the partial mass density ρ_t^F and to volume changes of the skeleton $J^S \approx 1 + \text{tr } \mathbf{e}^S$. We have

$$\varsigma = \frac{n}{n_0} - 1 \approx \frac{\rho_t^F - \rho_0^F}{\rho_0^F} + \text{tr } \mathbf{e}^S, \quad \rho_0^F \equiv n_0 \rho_0^{FR}.\tag{204}$$

The first contribution describes the macroscopic volume changes of the fluid component, i.e it is the (macroscopic) negative fluid *dilation* ε while the second contribution describes changes of the macroscopic volume e . Hence

$$\varsigma \approx e - \varepsilon, \quad e := \text{tr } \mathbf{e}^S, \quad \varepsilon := -\frac{\rho_t^F - \rho_0^F}{\rho_0^F} \implies \zeta = n_0 \varsigma.\tag{205}$$

Let us note that the macroscopic model constructed in this way does not require any reference to the microscopic description.

Before we proceed with the linearization of constitutive relations it is convenient to change the variables in (193) from (ρ^F, J^S) to (ρ_t^F, J^S) . Bearing identities of the previous Subsection in mind we obtain

$$\begin{aligned}\mathbf{T}^S &= \rho_t^S \left\{ J^S \frac{\partial \psi^S}{\partial J^S} + 2 \left(\frac{\partial \psi^S}{\partial I} + I \frac{\partial \psi^S}{\partial II} \right) \mathbf{B}^S - 2 \frac{\partial \psi^S}{\partial III} \mathbf{B}^S \right\} - n_0 N \frac{\rho_t^F}{\rho_0^F} \mathbf{1}, \\ \mathbf{T}^F &= - \left(\rho_t^{F2} \frac{\partial \psi^F}{\partial \rho_t^F} + n_0 N \frac{\rho_t^F}{\rho_0^F} \right) \mathbf{1}.\end{aligned}\quad (206)$$

Obviously the stress tensor in the skeleton possesses already the structure desired in the comparison to Biot's model. The last contribution can be written in terms of the variable ε which reflects the coupling with the fluid. Such a contribution does not appear in the stress tensor for the fluid. However the free energy ψ^F may be still dependent on both variables (ρ_t^F, J^S) . Consequently we can choose this dependence in such a way that the symmetry required by the Biot's model remains preserved. It is easy to check that the following choice

$$\psi^F = \psi_{ideal}^F(\rho_t^F) + n_0 N \frac{e}{\rho_t^F}, \quad N = const., \quad J^S \equiv 1 + e, \quad (207)$$

indeed yields the desired coupling and it is compatible with the relation (186) provided the coupling coefficient N in the fully nonlinear model possesses a specific dependence on volume changes of the skeleton J^S

$$N = \frac{N_0}{J^S}, \quad N_0 = const. \quad (208)$$

This yields indeed the relation (207) because in the linear model we do not have to distinguish between N and N_0 in the above relation. Such a dependence is solely motivated by the requirement of the linear model and cannot be derived from any thermodynamical relations.

Let us make an important observation that the coupling in the partial stress tensor \mathbf{T}^F cannot be corrected any more because the contribution ψ_{ideal}^F is independent of volume changes of the skeleton. Hence the coupling constant must be of the order of the constant N .

The standard linearization procedure leads now to the following linear constitutive relations for partial stresses

$$\begin{aligned}\mathbf{T}^S &= \mathbf{T}_0^S + \lambda^S e \mathbf{1} + 2\mu^S \mathbf{e}^S + n_0 N \varepsilon \mathbf{1}, \\ \mathbf{T}^F &= -p^F \mathbf{1}, \quad p^F := p_0^F - (R\varepsilon + n_0 N e),\end{aligned}\quad (209)$$

where \mathbf{T}_0^S, p_0^F are initial values of the stress in the skeleton: $\mathbf{F}^S = \mathbf{1}$, or equivalently $\mathbf{e}^S = \mathbf{0}$, as well as $\varepsilon = 0$, and of the partial pressure in the fluid, respectively. The material parameters λ^S, μ^S, R, N may depend solely on the initial porosity n_0 .

In order to obtain Biot's stress relations we have to identify $Q = n_0 N$ and to assume that initial stresses are zero (stresses in Biot's relations are the so-called excess stresses).

We have considered in this Section the simplest version of a linear higher gradient model but it is almost obvious that either contributions of relative velocities to free energies or nonlinear contributions of the gradient of porosity do not change anything in the structure of a linearized model.

8 Thermoporoelastic two-component materials with an influence of relative accelerations

8.1 Objective relative acceleration

Apart from the question of contribution of interactions in partial stress tensors there is another question connected with the classical Biot model of poroelastic materials. As proposed by Biot it is often assumed that momentum balance equations contain a contribution of relative accelerations. This yields the consequence that the matrix of partial mass densities is not diagonal. The off-diagonal part is assumed to be symmetric, i.e. this additional contribution is described by a material parameter ρ_{12} . It is easy to check that such a contribution violates the principle of material objectivity [65]. We show in this Section that one may construct a nonlinear model in which such a contribution becomes materially objective and reduces in the linear limit to the Biot contribution (for details see: [72]).

Such a nonlinear objective model with a contribution of relative accelerations is thermodynamically admissible if we add some nonlinear contributions to partial stresses and to the free energy. They reflect in the simplest manner the existence of fluctuations of the microstructural kinetic energy caused by the heterogeneity of momentum in the representative elementary volume. The existence of such fluctuations as a result of tortuosity of porous materials has been indicated by O. Coussy [16]. Kinematic considerations concerning a structure of such fluctuations are presented in the article of W. Kosinski, J. Kubik and K. Hutter [30]. Further quotations concerning this issue can be also found in this work. However the constitutive part of a model based on such considerations has not been presented. There exist some attempts to derive Biot's model with the contribution of relative acceleration by means of Hamilton's principle based on the fluctuation kinetic energy. As the true variational principle does not hold for dissipative systems the dissipation through fluctuation and diffusion is accounted for by a pseudo-potential and a pseudo-variational principle. This does not seem to be the right way of handling irreversible processes. For this reason we rely rather on the nonequilibrium thermodynamics in our considerations.

We consider a two-component continuum consisting of a solid skeleton and of a fluid. The motion of the skeleton is assumed to be described by the following twice continuously differentiable function

$$\mathbf{x} = \boldsymbol{\chi}^S(\mathbf{X}, t), \quad \mathbf{X} \in \mathcal{B}_0, \quad t \in \mathcal{T}, \quad (210)$$

where \mathcal{B}_0 denotes the reference configuration of the skeleton and \mathcal{T} is the time interval. The velocity, acceleration and the deformation gradient of the skeleton are defined by the relations

$$\dot{\mathbf{x}}^S := \frac{\partial \boldsymbol{\chi}^S}{\partial t}, \quad \ddot{\mathbf{x}}^S := \frac{\partial \dot{\mathbf{x}}^S}{\partial t}, \quad \mathbf{F}^S := \text{Grad } \boldsymbol{\chi}^S. \quad (211)$$

Certainly, the value $\mathbf{F}^S = \mathbf{1}$ corresponds to the reference configuration for, say, $t = t_0$ in which $\boldsymbol{\chi}^S(\mathbf{X}, t_0) = \mathbf{X}$.

The motion of the fluid is described by the transformation of the Eulerian velocity field $\mathbf{v}^F = \mathbf{v}^F(\mathbf{x}, t)$ defined on the space of current configurations $\chi^S(\mathcal{B}_0, t)$ of the skeleton. We have

$$\mathbf{v}^F = \mathbf{v}^F(\chi^S(\mathbf{X}, t), t) =: \dot{\mathbf{x}}^F(\mathbf{X}, t). \quad (212)$$

The acceleration of the fluid is then given by

$$\ddot{\mathbf{x}}^F = \frac{\partial \dot{\mathbf{x}}^F}{\partial t} + \dot{\mathbf{X}}^F \cdot \text{Grad } \dot{\mathbf{x}}^F, \quad \dot{\mathbf{X}}^F := \mathbf{F}^{S-1}(\dot{\mathbf{x}}^F - \dot{\mathbf{x}}^S), \quad (213)$$

where $\dot{\mathbf{X}}^F$ is the Lagrangian velocity of the fluid with respect to the skeleton.

We proceed to determine the transformation rules for the above quantities specified by the Euclidean transformation rule

$$\mathbf{x}^* = \mathbf{O}(t) \mathbf{x} + \mathbf{c}(t). \quad (214)$$

The relations (211) and the time differentiation of the relation (214) yield the following quantities in the new reference system

$$\mathbf{F}^{S*} = \mathbf{O} \mathbf{F}^S, \quad \dot{\mathbf{x}}^{S*} = \mathbf{O} \dot{\mathbf{x}}^S + \dot{\mathbf{O}} \mathbf{x} + \dot{\mathbf{c}}, \quad \ddot{\mathbf{x}}^{S*} = \mathbf{O} \ddot{\mathbf{x}}^S + 2\dot{\mathbf{O}} \dot{\mathbf{x}}^S + \ddot{\mathbf{O}} \mathbf{x} + \ddot{\mathbf{c}}, \quad (215)$$

where the dot denotes the time derivative.

We assume that the transformation rule for the velocity field of the fluid component has the same form as it does for the skeleton

$$\dot{\mathbf{x}}^{F*} = \mathbf{O} \dot{\mathbf{x}}^F + \dot{\mathbf{O}} \mathbf{x} + \dot{\mathbf{c}}. \quad (216)$$

Consequently

$$\dot{\mathbf{x}}^{F*} - \dot{\mathbf{x}}^{S*} = \mathbf{O}(\dot{\mathbf{x}}^F - \dot{\mathbf{x}}^S) \Rightarrow \dot{\mathbf{X}}^{F*} = \dot{\mathbf{X}}^F. \quad (217)$$

Bearing these relations in mind we can now easily derive the transformation of the acceleration of the fluid. We obtain immediately

$$\begin{aligned} \ddot{\mathbf{x}}^{F*} &= \frac{\partial}{\partial t} (\mathbf{O} \dot{\mathbf{x}}^F + \dot{\mathbf{O}} \mathbf{x} + \dot{\mathbf{c}}) + \dot{\mathbf{X}}^F \cdot \text{Grad} (\mathbf{O} \dot{\mathbf{x}}^F + \dot{\mathbf{O}} \mathbf{x} + \dot{\mathbf{c}}) = \\ &= \mathbf{O} \ddot{\mathbf{x}}^F + 2\dot{\mathbf{O}} \dot{\mathbf{x}}^F + \ddot{\mathbf{O}} \mathbf{x} + \ddot{\mathbf{c}}, \end{aligned} \quad (218)$$

where the definition of the Lagrangian velocity has been used.

Due to the presence of contributions dependent solely on the choice of the frame we say that velocities $\dot{\mathbf{x}}^S, \dot{\mathbf{x}}^F$ and accelerations $\ddot{\mathbf{x}}^S, \ddot{\mathbf{x}}^F$ are nonobjective. Consequently, their difference is also nonobjective. We have

$$\ddot{\mathbf{x}}^{F*} - \ddot{\mathbf{x}}^{S*} = \mathbf{O}(\ddot{\mathbf{x}}^F - \ddot{\mathbf{x}}^S) + 2\dot{\mathbf{O}}(\dot{\mathbf{x}}^F - \dot{\mathbf{x}}^S). \quad (219)$$

For this reason the difference of accelerations cannot be used as a constitutive variable in a construction of the macroscopic model of a two-component system.

In the paper [18] a method has been proposed to overcome these difficulties in the Eulerian description of suspensions. We shall use a similar way in the Lagrangian description. If we take the gradient of the transformation relations for velocities we obtain

$$\text{Grad } \dot{\mathbf{x}}^{S*} = \mathbf{O} \text{Grad } \dot{\mathbf{x}}^S + \dot{\mathbf{O}} \mathbf{F}^S \Rightarrow \dot{\mathbf{O}} = \text{Grad} (\dot{\mathbf{x}}^{S*} - \mathbf{O} \dot{\mathbf{x}}^S) \mathbf{F}^{S-1},$$

$$\text{Grad } \dot{\mathbf{x}}^{F*} = \mathbf{O} \text{Grad } \dot{\mathbf{x}}^F + \dot{\mathbf{O}} \mathbf{F}^S \Rightarrow \dot{\mathbf{O}} = \text{Grad } (\dot{\mathbf{x}}^{F*} - \mathbf{O} \dot{\mathbf{x}}^F) \mathbf{F}^{S-1}. \quad (220)$$

Consequently, we can write

$$\begin{aligned} 2\dot{\mathbf{O}} (\dot{\mathbf{x}}^F - \dot{\mathbf{x}}^S) &= (2 - \mathfrak{z}) \dot{\mathbf{O}} (\dot{\mathbf{x}}^F - \dot{\mathbf{x}}^S) + \mathfrak{z} \dot{\mathbf{O}} (\dot{\mathbf{x}}^F - \dot{\mathbf{x}}^S) = \\ &= (2 - \mathfrak{z}) \text{Grad } (\dot{\mathbf{x}}^{F*} - \mathbf{O} \dot{\mathbf{x}}^F) \dot{\mathbf{X}}^F + \mathfrak{z} \text{Grad } (\dot{\mathbf{x}}^{S*} - \mathbf{O} \dot{\mathbf{x}}^S) \dot{\mathbf{X}}^F, \end{aligned} \quad (221)$$

where \mathfrak{z} is arbitrary.

Substitution of this relation in (219) yields

$$\begin{aligned} \ddot{\mathbf{x}}^{F*} - \ddot{\mathbf{x}}^{S*} - (2 - \mathfrak{z}) \dot{\mathbf{X}}^F \cdot \text{Grad } \dot{\mathbf{x}}^{F*} - \mathfrak{z} \dot{\mathbf{X}}^F \cdot \text{Grad } \dot{\mathbf{x}}^{S*} &= \\ &= \mathbf{O} \left(\ddot{\mathbf{x}}^F - \ddot{\mathbf{x}}^S - (2 - \mathfrak{z}) \dot{\mathbf{X}}^F \cdot \text{Grad } \dot{\mathbf{x}}^F - \mathfrak{z} \dot{\mathbf{X}}^F \cdot \text{Grad } \dot{\mathbf{x}}^S \right). \end{aligned} \quad (222)$$

It means that the quantity

$$\begin{aligned} \mathbf{a}_r &:= \frac{\partial}{\partial t} (\dot{\mathbf{x}}^F - \dot{\mathbf{x}}^S) + \dot{\mathbf{X}}^F \cdot \text{Grad } \dot{\mathbf{x}}^F - (2 - \mathfrak{z}) \dot{\mathbf{X}}^F \cdot \text{Grad } \dot{\mathbf{x}}^F - \mathfrak{z} \dot{\mathbf{X}}^F \cdot \text{Grad } \dot{\mathbf{x}}^S \equiv \\ &\equiv \frac{\partial}{\partial t} (\dot{\mathbf{x}}^F - \dot{\mathbf{x}}^S) - (1 - \mathfrak{z}) \dot{\mathbf{X}}^F \cdot \text{Grad } \dot{\mathbf{x}}^F - \mathfrak{z} \dot{\mathbf{X}}^F \cdot \text{Grad } \dot{\mathbf{x}}^S, \end{aligned} \quad (223)$$

is objective, i.e.

$$\mathbf{a}_r^* = \mathbf{O} \mathbf{a}_r. \quad (224)$$

We call this quantity an *objective relative acceleration*. As an objective variable it can be incorporated into the set of constitutive variables. Obviously, there exists a class of such accelerations specified by the constitutive coefficient \mathfrak{z} .

It is easy to see that a linear momentum source $\hat{\mathbf{p}}$ in an isotropic material would contain a term $\rho_{12}^0 \mathbf{a}_r \approx \rho_{12}^0 \frac{\partial}{\partial t} (\dot{\mathbf{x}}^F - \dot{\mathbf{x}}^S)$ as required by the relations of Biot's model. The open question is if the second law of thermodynamics admits this type of contribution in a fully nonlinear model.

8.2 Thermodynamical admissibility

As we have already mentioned the nonlinear poroelastic two-component model requires the formulation of field equations for the following fields

$$\mathcal{V} := \{ \rho^F, \dot{\mathbf{x}}^S, \dot{\mathbf{x}}^F, \mathbf{F}^S, T, n \} \quad \text{for} \quad (\mathbf{X}, t) \in \mathcal{B}_0 \times \mathcal{T}, \quad (225)$$

where ρ^F is the partial mass density of the fluid per unit volume in the reference configuration of the skeleton, i.e. in the current configuration it is given by the relation $\rho_t^F = \rho^F J^{S-1}$, $J^S := \det \mathbf{F}^S$. T is the absolute temperature of the medium common for both components, and n is the current porosity. Other symbols have the same meaning as before.

The partial mass density of the skeleton in the reference configuration, ρ^S , does not appear among the fields because it is constant in a homogeneous material without mass exchange between components.

These fields are assumed again to fulfil the following set of balance equations

$$R^F := \frac{\partial \rho^F}{\partial t} + \text{Div} \left(\rho^F \dot{\mathbf{X}}^F \right) = 0, \quad (226)$$

$$\mathbf{M}^S := \rho^S \frac{\partial \dot{\mathbf{X}}^S}{\partial t} - \text{Div} \mathbf{P}^S - \hat{\mathbf{p}} = \mathbf{0}, \quad (227)$$

$$\mathbf{M}^F := \rho^F \left(\frac{\partial \dot{\mathbf{X}}^F}{\partial t} + \dot{\mathbf{X}}^F \cdot \text{Grad} \dot{\mathbf{X}}^F \right) - \text{Div} \mathbf{P}^F + \hat{\mathbf{p}} = \mathbf{0}, \quad (228)$$

$$\begin{aligned} E &: = \frac{\partial \rho \varepsilon}{\partial t} + \text{Div} \mathbf{Q} - \mathbf{P}^S \cdot \text{Grad} \dot{\mathbf{X}}^S - \mathbf{P}^F \cdot \text{Grad} \dot{\mathbf{X}}^F - (\mathbf{F}^{ST} \hat{\mathbf{p}}) \cdot \dot{\mathbf{X}}^F = 0, \\ \rho &: = \rho^S + \rho^F, \end{aligned} \quad (229)$$

$$\mathbf{F} := \frac{\partial \mathbf{F}^S}{\partial t} - \text{Grad} \dot{\mathbf{X}}^S = \mathbf{0}, \quad (230)$$

$$N := \frac{\partial \Delta_n}{\partial t} + \text{Div} \mathbf{J} - \hat{n} = 0, \quad \Delta_n := n - n_E, \quad (231)$$

where $\mathbf{P}^S, \mathbf{P}^F$ denote the first Piola-Kirchhoff partial stress tensors, $\hat{\mathbf{p}}$ is the momentum source, ε is the specific internal energy per unit mass of the mixture, \mathbf{Q} is the heat flux vector, n_E describes the so-called equilibrium porosity, \mathbf{J} is the porosity flux, and \hat{n} is the porosity source.

The porosity balance equation (231) yields the model essentially beyond the frame of Biot's model due to the contribution of relaxation source \hat{n} . It has been introduced some years ago [57] and analyzed in numerous papers. For instance, the applicability in the theory of abrasion has been discussed by N. Kirchner (e.g. [28]).

As we show in Section 10 changes of porosity predicted by the linearized porosity balance equation are identical with those following from Biot's model and Gassmann relations provided the relaxation time of porosity goes to infinity (i.e. $\hat{n} \equiv 0$). However, it should be mentioned that many other approaches to the problem of evolution of volume fractions, porosity, etc. appear in the literature. One of the most popular forms of such an evolution equation follows from the so-called principle of equilibrated pressures introduced by Goodman, Cowin, Nunziato, Passman and others (e.g. see [28] for references and discussion). Even though in some applications such an approach may be advantageous to the porosity balance, we do not discuss it any further in these notes.

In order to obtain field equations from the above balance equations we have to specify constitutive relations for these quantities, i.e

$$\mathcal{F} := \{ \mathbf{P}^S, \mathbf{P}^F, \hat{\mathbf{p}}, \varepsilon, \mathbf{Q}, n_E, \mathbf{J}, \hat{n} \}, \quad (232)$$

must be functions of constitutive variables. In this Section the set of constitutive variables is chosen as follows

$$\mathcal{C} := \left\{ \rho^F, \mathbf{F}^S, \dot{\mathbf{X}}^F, \Delta_n, T, \mathbf{G}, \mathbf{a}_r \right\}, \quad \mathbf{G} := \text{Grad} T. \quad (233)$$

Hence the gradient of porosity does not appear among the variables. It means that we can expect only a simple mixture model to follow from thermodynamic considerations. We do so on purpose to avoid technical difficulties of accounting simultaneously for two new contributions: due to \mathbf{a}_r and due to $\mathbf{N} := \text{Grad } n$. In the full model in which both contributions are present we use the results of thermodynamic considerations for two models considered separately. One can show that the combined model satisfies the second law of thermodynamics.

Once the function

$$\mathcal{F} = \mathcal{F}(\mathcal{C}), \quad (234)$$

is given, we obtain a closed system of differential equations for fields \mathcal{V} .

We say that constitutive relations (234) satisfy the **second law of thermodynamics** if the following entropy inequality

$$\frac{\partial \rho \eta}{\partial t} + \text{Div } \mathbf{H} \geq 0, \quad \eta = \eta(\mathcal{C}), \quad \mathbf{H} = \mathbf{H}(\mathcal{C}), \quad (235)$$

is satisfied by all solutions of field equations. In this inequality η is the specific entropy and \mathbf{H} its flux.

This requirement is equivalent to the following inequality which must hold for **all fields**

$$\frac{\partial \rho \eta}{\partial t} + \text{Div } \mathbf{H} - \Lambda^{\rho^F} R^F - \Lambda^{v^S} \cdot \mathbf{M}^S - \Lambda^{v^F} \cdot \mathbf{M}^F - \Lambda^\varepsilon E - \Lambda^F \cdot \mathbf{F} - \Lambda^n N \geq 0, \quad (236)$$

where

$$\Lambda^{\rho^F}, \Lambda^{v^S}, \Lambda^{v^F}, \Lambda^\varepsilon, \Lambda^F, \Lambda^n \quad (237)$$

are Lagrange multipliers dependent on constitutive variables \mathcal{C} .

The exploitation of the second law of thermodynamics in the general case is technically impossible. Therefore we make simplifying assumptions sufficient for the second law to be satisfied and yielding explicit limitations on constitutive relations. They are as follows:

1° The material is isotropic. Consequently, scalar constitutive functions, for instance, depend on vector and tensor variables solely through invariants. This assumption will be applied in some steps of our proofs. Some relations are simpler in a general form and then we do not introduce this limitation.

2° The dependence on the relative velocity $\dot{\mathbf{X}}^F$ is at most quadratic. This assumption is related to the structure of the nonlinear contribution to the objective relative acceleration. We motivate its form further.

3° The dependence on the temperature gradient \mathbf{G} is linear. We could skip this assumption on the cost of some technicalities but the experience with the thermodynamical construction of poroelastic models shows that it does not yield any undesired results.

4° The dependence on the deviation of porosity n from its equilibrium value n_E , $\Delta_n \equiv n - n_E$, is quadratic.

5° The dependence on the relative acceleration \mathbf{a}_r is linear.

6° Higher order combinations of variables $\mathbf{G}, \dot{\mathbf{X}}^F, \Delta_n, \mathbf{a}_r$ can be neglected.

As we see further these assumptions limit thermodynamical considerations to a vicinity of the thermodynamical equilibrium similar to this appearing in the classical Onsager thermodynamics.

Bearing these assumptions in mind we can write the following representations of constitutive functions

– partial stresses

$$\begin{aligned}\mathbf{P}^S &= \mathbf{P}_0^S(\mathcal{C}_E, \Delta_n) + \frac{1}{2}\sigma^S(\mathcal{C}_E) \mathbf{F}^S \dot{\mathbf{X}}^F \otimes \dot{\mathbf{X}}^F, \quad \mathcal{C}_E := \{\rho^F, \mathbf{F}^S, T\}, \\ \mathbf{P}^F &= \mathbf{P}_0^F(\mathcal{C}_E, \Delta_n) + \frac{1}{2}\sigma^F(\mathcal{C}_E) \mathbf{F}^S \dot{\mathbf{X}}^F \otimes \dot{\mathbf{X}}^F, \quad n_E = n_E(\mathcal{C}_E),\end{aligned}\tag{238}$$

– internal energy and entropy

$$\begin{aligned}\rho\varepsilon &= \rho\varepsilon_0(\mathcal{C}_E, \Delta_n) + \frac{1}{2}\varepsilon_d(\mathcal{C}_E) \left(\mathbf{F}^S \dot{\mathbf{X}}^F \right) \cdot \left(\mathbf{F}^S \dot{\mathbf{X}}^F \right), \\ \rho\eta &= \rho\eta_0(\mathcal{C}_E, \Delta_n) + \frac{1}{2}\eta_d(\mathcal{C}_E) \left(\mathbf{F}^S \dot{\mathbf{X}}^F \right) \cdot \left(\mathbf{F}^S \dot{\mathbf{X}}^F \right),\end{aligned}\tag{239}$$

– fluxes of energy, entropy, porosity

$$\begin{aligned}\mathbf{Q} &= Q_V \dot{\mathbf{X}}^F - K\mathbf{G} + Q_a \mathbf{F}^{ST} \mathbf{a}_r, \\ \mathbf{H} &= H_V \dot{\mathbf{X}}^F + H_T \mathbf{G} + H_a \mathbf{F}^{ST} \mathbf{a}_r, \\ \mathbf{J} &= \Phi \dot{\mathbf{X}}^F + J_T \mathbf{G} + J_a \mathbf{F}^{ST} \mathbf{a}_r,\end{aligned}\tag{240}$$

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

– momentum source

$$\mathbf{F}^{ST} \hat{\mathbf{p}} = \Pi_V \dot{\mathbf{X}}^F + \Pi_T \mathbf{G} - \rho_{12}^0 \mathbf{F}^{ST} \mathbf{a}_r,\tag{241}$$

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

The notation of some coefficients in the above relations corresponds to this which is customary in the literature.

The contributions with the coefficients ε_d, η_d to the energy and entropy are motivated by fluctuations of the microstructural kinetic energy caused by the tortuosity. We do not introduce any additional microstructural variable describing changes of tortuosity. For this reason a macroscopic influence of tortuosity can be solely reflected by the seepage velocity which in our model corresponds to the Lagrangian velocity $\dot{\mathbf{X}}^F$. The classical kinetic energy in this model is given by $\frac{1}{2}(\rho^S \dot{\mathbf{X}}^S \cdot \dot{\mathbf{X}}^S + \rho^F \dot{\mathbf{X}}^F \cdot \dot{\mathbf{X}}^F)$. Consequently, the correction $\frac{1}{2}\varepsilon_d(\dot{\mathbf{X}}^F - \dot{\mathbf{X}}^S) \cdot (\dot{\mathbf{X}}^F - \dot{\mathbf{X}}^S)$ may be considered as an **added mass effect** resulting from tortuosity.

As we see further, the dependence of partial stresses on this velocity, introduced in the simplest form by (238), is then required by the consistency of the model with the second law of thermodynamics. In other words, we show further that coefficients σ^S, σ^F in the stress relations (238) and the coefficient ε_d in the energy relation (239) are connected (see: formula (281)).

The exploitation of the second law of thermodynamics (236) is standard (e.g. see [34]). We apply the chain rule of differentiation to constitutive laws. We skip here rather cumbersome technical details.

Linearity of the second law of thermodynamics with respect to time derivatives

$$\left\{ \frac{\partial \rho^F}{\partial t}, \frac{\partial \mathbf{F}^S}{\partial t}, \frac{\partial \Delta_n}{\partial t}, \frac{\partial \dot{\mathbf{x}}^S}{\partial t}, \frac{\partial \dot{\mathbf{x}}^F}{\partial t}, \frac{\partial T}{\partial t}, \frac{\partial \mathbf{G}}{\partial t} \right\}$$

yields

$$\Lambda^{\rho^F} = \Lambda_0^{\rho^F} + \frac{1}{2} \left(\frac{\partial \eta_d}{\partial \rho^F} - \Lambda^\varepsilon \frac{\partial \varepsilon_d}{\partial \rho^F} \right) (\mathbf{F}^S \dot{\mathbf{x}}^F) \cdot (\mathbf{F}^S \dot{\mathbf{x}}^F), \quad (242)$$

$$\Lambda_0^{\rho^F} := \frac{\partial \rho \eta_0}{\partial \rho^F} - \Lambda^\varepsilon \frac{\partial \rho \varepsilon_0}{\partial \rho^F}$$

$$\Lambda^F = \frac{\partial \rho \eta_0}{\partial \mathbf{F}^F} - \Lambda^\varepsilon \frac{\partial \rho \varepsilon_0}{\partial \mathbf{F}^F} + \frac{1}{2} \left(\frac{\partial \eta_d}{\partial \mathbf{F}^F} - \Lambda^\varepsilon \frac{\partial \varepsilon_d}{\partial \mathbf{F}^F} \right) (\mathbf{F}^S \dot{\mathbf{x}}^F) \cdot (\mathbf{F}^S \dot{\mathbf{x}}^F), \quad (243)$$

$$\Lambda^n = \frac{\partial \rho \eta_0}{\partial \Delta_n} - \Lambda^\varepsilon \frac{\partial \rho \varepsilon_0}{\partial \Delta_n}, \quad (244)$$

$$(\rho^S - \rho_{12}^0) \Lambda^{v^S} + \rho_{12}^0 \Lambda^{v^F} = -(\eta_d - \Lambda^\varepsilon \varepsilon_d) \mathbf{F}^S \dot{\mathbf{x}}^F + \rho_{12}^0 \Lambda^\varepsilon \mathbf{F}^S \dot{\mathbf{x}}^F - \text{Div} (H_a \mathbf{F}^S) + \Lambda^\varepsilon \text{Div} (Q_a \mathbf{F}^S) + \Lambda^n \text{Div} (J_a \mathbf{F}^S) = 0, \quad (245)$$

$$(\rho^F - \rho_{12}^0) \Lambda^{v^F} + \rho_{12}^0 \Lambda^{v^S} = (\eta_d - \Lambda^\varepsilon \varepsilon_d) \mathbf{F}^S \dot{\mathbf{x}}^F - \rho_{12}^0 \Lambda^\varepsilon \mathbf{F}^S \dot{\mathbf{x}}^F + \text{Div} (H_a \mathbf{F}^S) - \Lambda^\varepsilon \text{Div} (Q_a \mathbf{F}^S) - \Lambda^n \text{Div} (J_a \mathbf{F}^S) = 0, \quad (246)$$

$$\frac{\partial \rho \eta_0}{\partial T} - \Lambda^\varepsilon \frac{\partial \rho \varepsilon_0}{\partial T} + \frac{1}{2} \left(\frac{\partial \eta_d}{\partial T} - \Lambda^\varepsilon \frac{\partial \varepsilon_d}{\partial T} \right) (\mathbf{F}^S \dot{\mathbf{x}}^F) \cdot (\mathbf{F}^S \dot{\mathbf{x}}^F) = 0. \quad (247)$$

These identities still contain linear contributions of $\text{Grad } \mathbf{F}^S$, Δ_n , quadratic contributions of the latter as well as quadratic contributions of Lagrangian velocity. As they should hold for arbitrary fields coefficients of these contributions must vanish separately. After easy analysis we obtain

$$H_a = 0, \quad Q_a = 0, \quad J_a = 0, \quad (248)$$

$$\rho^S \Lambda^{v^S} = -\rho^F \Lambda^{v^F} = \eta \mathbf{F}^S \dot{\mathbf{x}}^F, \quad \eta := -\frac{\eta_d - \Lambda^\varepsilon \varepsilon_d - \Lambda^\varepsilon \rho_{12}^0}{\rho^S - \rho_{12}^0 \left(1 + \frac{\rho^S}{\rho^F} \right)}. \quad (249)$$

The second law of thermodynamics is also linear with respect to the following spatial derivatives

$$\text{Grad } \dot{\mathbf{x}}^S, \text{Grad } \dot{\mathbf{x}}^F, \text{Grad } \rho^F, \text{Grad } \mathbf{F}^S, \text{Grad } \mathbf{G}, \text{Grad } \Delta_n. \quad (250)$$

We have listed them in the order of the further analysis and, simultaneously, skipped the derivative $\text{Grad } \mathbf{a}_r$ because it does not contribute to the second law due to the relations (248). The linearity with respect to (250) yields a set of identities and leaves a residual

inequality which is essentially nonlinear. It defines the **dissipation** in the system and has the following form

$$\begin{aligned} \mathcal{D} := & \left(\frac{\partial H_V}{\partial T} - \Lambda^\varepsilon \frac{\partial Q_V}{\partial T} - \Lambda^n \frac{\partial \Phi}{\partial T} + \Pi_T \right) \dot{\mathbf{X}}^F \cdot \mathbf{G} + \\ & + \left(\frac{\partial H_T}{\partial T} + \Lambda^\varepsilon \frac{\partial K}{\partial T} - \Lambda^n \frac{\partial J_T}{\partial T} \right) \mathbf{G} \cdot \mathbf{G} + \\ & + \Lambda^\varepsilon \Pi_V \dot{\mathbf{X}}^F \cdot \dot{\mathbf{X}}^F + \Lambda^n \hat{n} \geq 0. \end{aligned} \quad (251)$$

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

$$\mathbf{G} = 0, \quad \dot{\mathbf{X}}^F = 0, \quad \hat{n} = 0, \quad (252)$$

i.e. the temperature gradient, relative motion (diffusion), and the relaxation of porosity cause the deviation from the equilibrium.

Clearly the assumption 4° yields the linearity of \hat{n} and Λ^n with respect to Δ_n . In addition, the above inequality yields homogeneity of these functions, i.e. we can write

$$\hat{n} = -\frac{\Delta_n}{\tau}, \quad \Lambda^n = \lambda^n \Delta_n, \quad (253)$$

where τ, λ^n can be solely functions of variables \mathcal{C}_E . Consequently, we obtain as well

$$\frac{\partial \Phi}{\partial T} = 0, \quad \frac{\partial J_T}{\partial T} = 0. \quad (254)$$

It is worth mentioning that due to (248) the relative acceleration does not contribute to the dissipation. This property of the model follows from the fact that the model does not possess any independent field of tortuosity which could relax to the thermodynamical equilibrium.

Now we return to the coefficients of spatial derivatives of fields. The vanishing coefficient of $\text{Grad } \dot{\mathbf{X}}^S$ yields the following results

$$\Lambda^\varepsilon \mathbf{P}_0^S \mathbf{F}^{ST} + \left(\frac{\partial \rho \eta_0}{\partial \mathbf{F}^S} - \Lambda^\varepsilon \frac{\partial \rho \varepsilon_0}{\partial \mathbf{F}^S} \right) \mathbf{F}^{ST} + \left(-H_V + \Lambda^\varepsilon Q_V + \Lambda^n \Phi + \rho^F \Lambda_0^{\rho^F} \right) \mathbf{1} = 0, \quad (255)$$

$$\frac{\partial \eta_d}{\partial I} - \Lambda^\varepsilon \frac{\partial \varepsilon_d}{\partial I} = 0, \quad \frac{\partial \eta_d}{\partial II} - \Lambda^\varepsilon \frac{\partial \varepsilon_d}{\partial II} = 0, \quad (256)$$

$$2 \left(\frac{\partial \eta_d}{\partial III} - \Lambda^\varepsilon \frac{\partial \varepsilon_d}{\partial III} \right) III + \rho^F \left(\frac{\partial \eta_d}{\partial \rho^F} - \Lambda^\varepsilon \frac{\partial \varepsilon_d}{\partial \rho^F} \right) = \mathfrak{y} \left(\sigma^S + \frac{\rho^S}{\rho^F} \sigma^F \right), \quad (257)$$

$$\mathfrak{z} = -\frac{1}{2\rho_{12}^0} \frac{\sigma^S \Lambda^\varepsilon - \mathfrak{y} \left(\sigma^S + \frac{\rho^S}{\rho^F} \sigma^F \right)}{\mathfrak{y} \left(1 + \frac{\rho^S}{\rho^F} \right) + \Lambda^\varepsilon}, \quad (258)$$

where

$$I := \text{tr } \mathbf{C}^S, \quad II := \frac{1}{2} (I^2 - \text{tr } \mathbf{C}^S), \quad III := \det \mathbf{C}^S, \quad \mathbf{C}^S := \mathbf{F}^{ST} \mathbf{F}^S, \quad (259)$$

are main invariants of the Cauchy-Green deformation tensor \mathbf{C}^S .

The coefficient of $\text{Grad } \dot{\mathbf{x}}^F$ yields

$$\Lambda^\varepsilon (\mathbf{P}_0^S + \mathbf{P}_0^F) = - \left(\frac{\partial \rho \eta_0}{\partial \mathbf{F}^S} - \Lambda^\varepsilon \frac{\partial \rho \varepsilon_0}{\partial \mathbf{F}^S} \right), \quad (260)$$

$$\frac{\partial \eta_d}{\partial III} - \Lambda^\varepsilon \frac{\partial \varepsilon_d}{\partial III} = 0, \quad (261)$$

$$\frac{1}{2} \Lambda^\varepsilon (\sigma^S + \sigma^F) = -\rho_{12}^0 \left(1 + \frac{\rho^S}{\rho^F} \right) \mathfrak{y} - \rho^S \mathfrak{y} - \rho_{12}^0 \Lambda^\varepsilon. \quad (262)$$

Consequently, bearing (256) and (261) in mind,

$$\frac{\partial \eta_d}{\partial \mathbf{F}^S} - \Lambda^\varepsilon \frac{\partial \varepsilon_d}{\partial \mathbf{F}^S} = 0. \quad (263)$$

Next we consider the coefficient of $\text{Grad } \rho^F$. We have

$$\left(\frac{\partial H_V}{\partial \rho^F} - \Lambda^\varepsilon \frac{\partial Q_V}{\partial \rho^F} - \Lambda^n \frac{\partial \Phi}{\partial \rho^F} - \Lambda^{\rho^F} \right) \dot{\mathbf{x}}^F + \mathfrak{y} \frac{\partial \mathbf{P}^{ST}}{\partial \rho^F} \mathbf{F}^S \dot{\mathbf{x}}^F - \mathfrak{y} \frac{\rho^F}{\rho^S} \frac{\partial \mathbf{P}^{FT}}{\partial \rho^F} \mathbf{F}^S \dot{\mathbf{x}}^F = 0, \quad (264)$$

$$\frac{\partial H_T}{\partial \rho^F} + \Lambda^\varepsilon \frac{\partial K}{\partial \rho^F} = 0, \quad \frac{\partial J_T}{\partial \rho^F} = 0. \quad (265)$$

Similarly, the coefficient of $\text{Grad } \mathbf{F}^S$ yields

$$\begin{aligned} & \text{sym} \left\{ \left(\frac{\partial H_V}{\partial \mathbf{F}^S} - \Lambda^\varepsilon \frac{\partial Q_V}{\partial \mathbf{F}^S} - \Lambda^n \frac{\partial \Phi}{\partial \mathbf{F}^S} \right) \otimes \dot{\mathbf{x}}^F + \rho^F \Lambda^{\rho^F} \mathbf{F}^{S-T} \otimes \dot{\mathbf{x}}^F + \mathfrak{y} \Xi^S + \mathfrak{y} \Xi^F \right\} - \\ & - \text{sym} \left\{ (H_V - \Lambda^\varepsilon - \Lambda^n \Phi) \mathbf{F}^{S-T} \otimes \dot{\mathbf{x}}^F \right\} = 0, \end{aligned} \quad (266)$$

$$\frac{\partial H_T}{\partial \mathbf{F}^S} + \Lambda^\varepsilon \frac{\partial K}{\partial \mathbf{F}^S} = 0, \quad \frac{\partial J_T}{\partial \mathbf{F}^S} = 0, \quad (267)$$

where the components of tensors Ξ^S, Ξ^F in Cartesian coordinates are given by the relations

$$\Xi_{kKL}^S = \frac{\partial P_{0LL}^S}{\partial F_{kK}^S} F_{lM}^S \dot{X}_M^F, \quad \Xi_{kKL}^F = -\frac{\rho^S}{\rho^F} \frac{\partial P_{0LL}^F}{\partial F_{kK}^S} F_{lM}^S \dot{X}_M^F. \quad (268)$$

Under our assumptions the contribution of $\text{Grad } \Delta_n$ does not yield any restrictions.

Finally, the last condition follows from the vanishing coefficient of $\text{Grad } \mathbf{G}$ and it has the form

$$H_T + \Lambda^\varepsilon K = 0, \quad J_T = 0. \quad (269)$$

Inspection of the results (265), (267) for thermal coefficients yields

$$\Lambda^\varepsilon = \Lambda^\varepsilon(T) \quad \Rightarrow \quad \Lambda^\varepsilon = \frac{1}{T}, \quad \text{i.e.} \quad H_T = -\frac{K}{T}, \quad (270)$$

where the ideal wall argument been used.

It is not quite clear what limitations on partial stress tensors are imposed by conditions (264), (266). Derivatives of partial stresses with respect to the mass density ρ^F as well as with respect to the deformation gradient \mathbf{F}^S seem to restrict elastic properties of the system in equilibrium. This does not seem very plausible. Hence we assume that the coefficient η vanishes, i.e.

$$\eta = 0. \quad (271)$$

Then the multipliers of momentum equations vanish as well. As the consequence of (247), (249), (257), (263) we obtain

$$-\rho_{12}^0 = \varepsilon_d - T\eta_d = \text{const.} \quad \Rightarrow \quad \varepsilon_d = \text{const.}, \quad \eta_d = 0. \quad (272)$$

It is convenient to introduce the following notation

$$\begin{aligned} \psi &:= \varepsilon - T\eta, \\ \rho\psi_0 &:= \rho\psi - \frac{1}{2}\varepsilon_d \left(\mathbf{F}^S \dot{\mathbf{X}}^F \right) \cdot \left(\mathbf{F}^S \dot{\mathbf{X}}^F \right). \end{aligned} \quad (273)$$

Then, for Lagrange multipliers we have

$$\Lambda^{\rho^F} = -\frac{1}{T} \frac{\partial \rho\psi_0}{\partial \rho^F} = \Lambda_0^{\rho^F}, \quad \Lambda^F = -\frac{1}{T} \frac{\partial \rho\psi_0}{\partial \mathbf{F}^S}, \quad \Lambda^n = -\frac{1}{T} \frac{\partial \rho\psi_0}{\partial \Delta_n} = \lambda^n \Delta_n, \quad (274)$$

and the relation (247) implies the following classical formula for the internal energy

$$\varepsilon = \psi - T \frac{\partial \psi}{\partial T}. \quad (275)$$

Simultaneously the relations (264), (266) yield

$$\begin{aligned} \frac{\partial H_V}{\partial \rho^F} - \Lambda^\varepsilon \frac{\partial Q_V}{\partial \rho^F} - \Lambda^{\rho^F} &= 0, \quad \frac{\partial \Phi}{\partial \rho^F} = 0, \\ 2III \left(\frac{\partial H_V}{\partial III} - \Lambda^\varepsilon \frac{\partial Q_V}{\partial III} \right) + \rho^F \Lambda^{\rho^F} - (H_V - \Lambda^\varepsilon Q_V) &= 0, \end{aligned} \quad (276)$$

$$2III \frac{\partial \Phi}{\partial III} - \Phi = 0 \quad \Rightarrow \quad \Phi = J^S \Phi_0, \quad \Phi_0 = \text{const.} \quad (277)$$

These relations yield the following integrability condition for the multiplier Λ^{ρ^F}

$$\rho^F \frac{\partial \Lambda^{\rho^F}}{\partial \rho^F} + J^S \frac{\partial \Lambda^{\rho^F}}{\partial J^S} = 0 \quad \Rightarrow \quad \Lambda^{\rho^F} = \Lambda^{\rho^F}(T, \rho_t^F), \quad \rho_t^F := J^{S-1} \rho^F. \quad (278)$$

Consequently, integration of (274)₁ leads to the following additive splitting of the free energy ψ

$$\begin{aligned} \rho\psi &= \rho^F \psi^F + \rho^S \psi^S - \frac{1}{2} \lambda^n T \Delta_n^2 + \frac{1}{2} \varepsilon_d \left(\mathbf{F}^S \dot{\mathbf{X}}^F \right) \cdot \left(\mathbf{F}^S \dot{\mathbf{X}}^F \right), \\ \psi^F &= \psi^F(T, \rho_t^F), \quad \psi^S = \psi^S(T, \mathbf{F}^S). \end{aligned} \quad (279)$$

The above separation property is characteristic for the so-called **simple mixtures**.

In addition, integration in (276)₁ yields

$$H_V - \frac{Q_V}{T} = -\frac{\rho^F \psi^F}{T}, \quad \text{i.e.} \quad \mathbf{H} = \frac{1}{T} \left(\mathbf{Q} - \rho^F \psi^F \dot{\mathbf{X}}^F \right), \quad (280)$$

where we have accounted for the relations (269) and (270).

Inspection of relations (272), (258) and (262) leads immediately to the following identification of constitutive coefficients coupled to the relative acceleration

$$\varepsilon_d = -\rho_{12}^0, \quad \sigma^S = -2\mathfrak{z}\rho_{12}^0, \quad \sigma^F = -2(1 - \mathfrak{z})\rho_{12}^0. \quad (281)$$

Simultaneously, relation (255) with (273), (274), (279) and (280) for partial stresses \mathbf{P}_0^S and relation (260) for partial stresses \mathbf{P}_0^F yield

$$\begin{aligned} \mathbf{P}^S &= \frac{\partial \rho^S \psi^S}{\partial \mathbf{F}^S} + \beta \Delta_n J^S \mathbf{F}^{S-T} - \mathfrak{z} \rho_{12}^0 \mathbf{F}^S \dot{\mathbf{X}}^S \otimes \dot{\mathbf{X}}^S, \quad \beta := T \lambda^n \Phi_0 J^{S-1}, \\ \mathbf{P}^F &= -\rho_t^{F2} \frac{\partial \psi^F}{\partial \rho_t^F} J^S \mathbf{F}^{S-T} - \beta \Delta_n J^S \mathbf{F}^{S-T} - (1 - \mathfrak{z}) \rho_{12}^0 \mathbf{F}^S \dot{\mathbf{X}}^S \otimes \dot{\mathbf{X}}^S. \end{aligned} \quad (282)$$

Hence, as mentioned in the introduction, the partial stresses do not possess a coupling term characteristic for Biot's model and this fallacy of the model can be removed by additional constitutive variables.

For practical purposes it is convenient to transform equations of the model to **Eulerian coordinates**. We write them in an arbitrary **noninertial** reference system. The set of balance equations (226) has then the form

– mass balance for the fluid component

$$\frac{\partial \rho_t^F}{\partial t} + \operatorname{div} (\rho_t^F \mathbf{v}^F) = 0, \quad (283)$$

– momentum balance for the skeleton

$$\begin{aligned} \rho_t^S \left(\frac{\partial \mathbf{v}^S}{\partial t} + \mathbf{v}^S \cdot \operatorname{grad} \mathbf{v}^S \right) &= \operatorname{div} \mathbf{T}^S + \rho_t^S \mathbf{b}^S + J^{S-1} \Pi_T \operatorname{grad} \mathbf{T} + \pi (\mathbf{v}^F - \mathbf{v}^S) - \\ &- \rho_{12} \left[\frac{\partial}{\partial t} (\mathbf{v}^F - \mathbf{v}^S) - (1 - \mathfrak{z}) (\mathbf{v}^F - \mathbf{v}^S) \cdot \operatorname{grad} \mathbf{v}^F - \mathfrak{z} (\mathbf{v}^F - \mathbf{v}^S) \cdot \operatorname{grad} \mathbf{v}^S \right], \end{aligned} \quad (284)$$

– momentum balance for the fluid

$$\begin{aligned} \rho_t^F \left(\frac{\partial \mathbf{v}^F}{\partial t} + \mathbf{v}^F \cdot \operatorname{grad} \mathbf{v}^F \right) &= \operatorname{div} \mathbf{T}^F + \rho_t^F \mathbf{b}^F - J^{S-1} \Pi_T \operatorname{grad} \mathbf{T} - \pi (\mathbf{v}^F - \mathbf{v}^S) + \\ &+ \rho_{12} \left[\frac{\partial}{\partial t} (\mathbf{v}^F - \mathbf{v}^S) - (1 - \mathfrak{z}) (\mathbf{v}^F - \mathbf{v}^S) \cdot \operatorname{grad} \mathbf{v}^F - \mathfrak{z} (\mathbf{v}^F - \mathbf{v}^S) \cdot \operatorname{grad} \mathbf{v}^S \right], \end{aligned} \quad (285)$$

– energy balance

$$\frac{\partial \rho_t \varepsilon}{\partial t} + \operatorname{div} (\rho_t \varepsilon \mathbf{v}^S + \mathbf{q}) - \mathbf{T}^S \cdot \operatorname{grad} \mathbf{v}^S - \mathbf{T}^F \cdot \operatorname{grad} \mathbf{v}^F - \quad (286)$$

$$\begin{aligned}
& - (\mathbf{v}^F - \mathbf{v}^S) \cdot \left\{ \pi (\mathbf{v}^F - \mathbf{v}^S) + J^{S-1} \Pi_T \text{grad } T - \right. \\
& \left. - \rho_{12} \left[\frac{\partial}{\partial t} (\mathbf{v}^F - \mathbf{v}^S) - (1 - \mathfrak{z}) (\mathbf{v}^F - \mathbf{v}^S) \cdot \text{grad } \mathbf{v}^F - \mathfrak{z} (\mathbf{v}^F - \mathbf{v}^S) \cdot \text{grad } \mathbf{v}^S \right] \right\}, \\
& - \text{porosity balance}
\end{aligned}$$

$$\frac{\partial J^{S-1} \Delta_n}{\partial t} + \text{div} (J^{S-1} \Delta_n \mathbf{v}^S + \mathbf{j}) + \frac{J^{S-1} \Delta_n}{\tau} = 0. \quad (287)$$

The external forces $\rho_t^S \mathbf{b}^S, \rho_t^F \mathbf{b}^F$, called **apparent body forces**, contributing to momentum balance equations have the following structure

$$\begin{aligned}
\rho_t^S \mathbf{b}^S &= \rho_t^S (\mathbf{b}_b^S + \mathbf{i}^S), \quad \rho_t^F \mathbf{b}^F = \rho_t^F (\mathbf{b}_b^F + \mathbf{i}^F), \\
\mathbf{i}^S &:= \ddot{\mathbf{c}} + 2\boldsymbol{\Omega} (\mathbf{v}^S - \dot{\mathbf{c}}) + (\dot{\boldsymbol{\Omega}} - \boldsymbol{\Omega}^2) (\mathbf{x} - \mathbf{c}), \\
\mathbf{i}^F &:= \ddot{\mathbf{c}} + 2\boldsymbol{\Omega} (\mathbf{v}^F - \dot{\mathbf{c}}) + (\dot{\boldsymbol{\Omega}} - \boldsymbol{\Omega}^2) (\mathbf{x} - \mathbf{c}), \quad \boldsymbol{\Omega} := \dot{\mathbf{O}} \mathbf{O}^T \equiv -\boldsymbol{\Omega}^T,
\end{aligned} \quad (288)$$

where $\rho_t^S \mathbf{b}_b^S, \rho_t^F \mathbf{b}_b^F$ are true (e.g. gravitational) body forces, and $\rho_t^S \mathbf{i}^S, \rho_t^F \mathbf{i}^F$ are called **inertial body forces**. In order of appearance in the above relations, they consist of the inertial force of relative translation, Coriolis force, Euler force, centrifugal force. They depend on the matrix of angular velocity $\boldsymbol{\Omega}$ of the noninertial system with respect to an inertial one. Certainly, the inertial body forces vanish in an inertial reference system. It should be mentioned that the partial accelerations appearing in the above partial momentum balance equations combined with apparent body forces are objective, i.e. invariant with respect to the Euclidean transformation.

The remaining notation used above is as follows

$$\rho_t^S = \rho^S J^{S-1}, \quad \rho_t = \rho_t^S + \rho_t^F, \quad \rho_{12} = \rho_{12}^0 J^{S-1}, \quad \pi = \Pi_V J^{S-1}, \quad (289)$$

while the Cauchy stress tensors $\mathbf{T}^S, \mathbf{T}^F$ are given by the following constitutive relations

$$\mathbf{T}^S = J^{S-1} \mathbf{P}^S \mathbf{F}^{ST} = 2\rho_t^S \left[\frac{\partial \psi^S}{\partial I} \mathbf{B}^S + \frac{\partial \psi^S}{\partial II} (I\mathbf{1} - \mathbf{B}^S) \mathbf{B}^S + \frac{\partial \psi^S}{\partial III} III \mathbf{1} \right] + \quad (290)$$

$$+ \beta \Delta_n \mathbf{1} - \mathfrak{z} \rho_{12} (\mathbf{v}^F - \mathbf{v}^S) \otimes (\mathbf{v}^F - \mathbf{v}^S), \quad \mathbf{B}^S = \mathbf{F}^S \mathbf{F}^{ST},$$

$$\mathbf{T}^F = J^{S-1} \mathbf{P}^F \mathbf{F}^{ST} = -p^F \mathbf{1} - \beta \Delta_n \mathbf{1} - (1 - \mathfrak{z}) \rho_{12} (\mathbf{v}^F - \mathbf{v}^S) \otimes (\mathbf{v}^F - \mathbf{v}^S) \quad (291)$$

$$p^F = \rho_t^{F2} \frac{\partial \psi^F}{\partial \rho_t^F},$$

with the free energy given by

$$\rho_t \psi = \rho_t^S \psi^S (T, I, II, III) + \rho_t^F \psi^F (T, \rho_t^F) - \rho_{12} (\mathbf{v}^F - \mathbf{v}^S) \cdot (\mathbf{v}^F - \mathbf{v}^S). \quad (292)$$

The energy ε and the energy flux vector \mathbf{q} are given by

$$\varepsilon = \psi - T \frac{\partial \psi}{\partial T}, \quad \mathbf{q} = J^{S-1} \mathbf{F}^S \mathbf{Q} = J^{S-1} Q_V (\mathbf{v}^F - \mathbf{v}^S) - J^{S-1} K \text{grad } T, \quad (293)$$

and the porosity flux has the form

$$\mathbf{j} = J^{S-1} \mathbf{F}^S \mathbf{J} = \Phi_0 (\mathbf{v}^F - \mathbf{v}^S). \quad (294)$$

It is easy to see that the linearization of the above set for isothermal processes without the source of porosity leads to Biot's equations (194) without the coupling constant Q .

There remains the question of practical estimation of additional parameters ρ_{12}^0 and \mathfrak{z} . The added mass coefficient ρ_{12}^0 has been extensively studied in literature concerning Biot's model. The parameter \mathfrak{z} is new. There seem to exist various possibilities for its estimation connected to the fact that it appears in contributions which may be time independent. As an example let us consider a stationary isothermal process in which, in a chosen inertial frame of reference, the skeleton does not move (i.e. $\mathbf{v}^S = 0$). Such a flow of the fluid through a porous material is described by the mass balance and by the momentum balance for the fluid. For simplicity we neglect changes of porosity. Then we have

$$\operatorname{div} (\rho_t^F \mathbf{v}^F) = 0, \quad (295)$$

$$\begin{aligned} [\rho_t^F + 2(1 - \mathfrak{z}) \rho_{12}] \mathbf{v}^F \cdot \operatorname{grad} \mathbf{v}^F &= -\operatorname{grad} p^F - [\pi + (1 - \mathfrak{z}) \rho_{12} \operatorname{div} \mathbf{v}^F] \mathbf{v}^F, \\ p^F &= p^F(\rho_t^F). \end{aligned}$$

The correction of the permeability coefficient π driven by volume changes of the fluid $\operatorname{div} \mathbf{v}^F$ seems to be very small. However the correction of mass density appearing on the left-hand side of this equation may be essential and measurable. For instance, in an irrotational flow ($\operatorname{rot} \mathbf{v}^F = 0$) we have approximately

$$\operatorname{grad} \left[n_0 (p - p_0) + \frac{1}{2} (\rho_t^F + 2(1 - \mathfrak{z}) \rho_{12}) \mathbf{v}^F \cdot \mathbf{v}^F \right] + \pi \mathbf{v}^F = 0, \quad (296)$$

where $p = p^F/n$ is the pore pressure and p_0 its constant reference value. If the pressure increment is of the order of, say, 10 kPa the velocity of the fluid must be of the order of 1 m/s to make both contributions of the similar order. Practically measurable would be the influence of \mathfrak{z} for much smaller velocities which seem to be plausible at least for rocks.

9 On macroscopic compressibility coefficients, Gassmann-like relations of linear poroelastic models

9.1 Introduction

In this Section we rely on an extended linear model of two-component poroelastic material and compare it with Biot's model [70]. This extended model contains the balance equation for porosity discussed in previous Sections of these notes as well as the constitutive dependence on the porosity gradient. We show that the balance equation of porosity can be solved approximately and the solution agrees with rather intuitive results of soil mechanics. Bearing this in mind, one can exploit certain Gedankenexperiments and the following generalization of Gassmann relations shows that Biot's model is one of the admissible solutions of the micro-macro transition problem for the thermodynamical model with the gradient of porosity. In addition, it follows as well that a "simple mixture" model of porous materials, developed earlier (e.g. [59], [74], [7], [4], [73]) is a reasonable approximation of both Biot's model and the thermodynamical model with porosity gradient in application to analysis of acoustic waves.

We proceed in the following way.

In Subsect. 2 we present a macroscopic linear poroelastic model of fully saturated, two-component media. All quantities appearing in this model have purely macroscopic, smeared-out interpretation. They are fields defined on a certain chosen constant domain of the three-dimensional configuration space. This means that they are functions of two variables: spatial position \mathbf{x} and time t . As in the classical theory of mixtures, in each point \mathbf{x} there appear both components of the system. This issue is important particularly in connection with frequent misunderstandings between those, who work in the frame of continuum approach and those, who work within classical soil mechanics with real grains and real fluids filling the channels. We return to this point in Subsect. 3.

Subsect. 3 is devoted to a particular class of static deformations described by the general two-component model – spherical deformations. In such cases components change solely their partial volumes but there is no shearing. This class is important for the exploitation of the so-called Gedankenexperiments. In the same Subsection we introduce Biot's notation for material parameters. The most important issue discussed in this Subsection is the micro-macro transition. Under the assumption of homogeneity of the microstructure we demonstrate two classes of compatibility relations of a continuum macroscopic two-component model and a microscopic model of two true components. We show that a condition for partial stress tractions yields two dynamical compatibility relations and the homogeneity of microstructure yields two geometrical compatibility relations.

The set of relations consisting of a single equilibrium condition (static equilibrium in spherical deformation processes), four compatibility relations, two constitutive relations on micro- and two on macrolevel yields the solution of any static spherical homogeneous problem.

In Subsect. 4 we present the so-called Gedankenexperiments. These are jacketed undrained, jacketed drained andunjacketed simple tests. They give rise to three additional relations. Together with the definition of the drained compressibility modulus K_d which is assumed to be given either experimentally or heuristically, we obtain four relations

which specify a dependence of four macroscopic material parameters $\{K, M, C, N\}$ on two microscopic compressibility moduli $\{K_s, K_f\}$ as well as on the initial porosity n_0 and the drained compressibility modulus K_d . Here we use Biot's notation and denote by K the bulk compressibility modulus of the skeleton, M is the compressibility modulus of the fluid, C is the coupling parameter which characterizes the influence of partial volume changes of one component on the pressure of the other component, and, finally, N denotes the parameter responsible for the coupling through the porosity gradient.

By means of the micro-macro transition procedure we obtain four algebraic relations for four material parameters which we solve numerically. One of those solutions contains the value $N \equiv 0$ which corresponds to classical Gassmann relations derived for the Biot model.

The most important conclusion of the work is that, in spite of flaws of both Biot's model and classical Gassmann relations, they follow from the full thermodynamical model in the linear approximation as an admissible possibility. This statement should be qualified by the fact that Gedankenexperiments may be the right way to describe the microstructure of granular materials but it does not seem to be appropriate for rocks. In such materials the coupling through the porosity gradient may be stronger and this would be a reason to ignore models in which the coefficient N vanishes. This is, certainly, also the case in nonlinear materials such as clays or biological tissues where one should rather apply the full thermodynamical model.

The procedure of micro-macro transition used in the present work as a method of derivation of Gassmann-type relations has an advantage in comparison with classical *ad hoc* methods that it can be easily extended to more complicated problems. In particular, we investigate in a forthcoming paper similar relations for unsaturated poroelastic materials.

9.2 Linear model

The linear poroelastic two-component model of isothermal processes in porous materials is based on the following set of unknown fields

$$\{\rho^S, \rho^F, \mathbf{v}^S, \mathbf{v}^F, \mathbf{e}^S, n\}, \quad (297)$$

where ρ^S, ρ^F are macroscopic current partial mass densities of the skeleton and of the fluid, respectively, $\mathbf{v}^S, \mathbf{v}^F$ are macroscopic velocity fields of these components, \mathbf{e}^S is the macroscopic deformation tensor and n denotes the current porosity, i.e. the fraction of the volume of voids in a chosen representative elementary volume (REV) to the corresponding total volume of REV. These fields must satisfy the following conditions which are the basis for the linearization of a nonlinear thermodynamical model

$$\max \left\{ \|\mathbf{e}^S\|, |\varepsilon|, \left| \frac{n - n_0}{n_0} \right| \right\} \ll 1, \quad (298)$$

$$\|\mathbf{e}^S\| := \max \{ |\lambda^{(1)}|, |\lambda^{(2)}|, |\lambda^{(3)}| \}, \quad \varepsilon := \frac{\rho_0^F - \rho^F}{\rho_0^F}, \quad (299)$$

where $\lambda^{(1)}, \lambda^{(2)}, \lambda^{(3)}$ are eigenvalues of the deformation tensor \mathbf{e}^S .

Fields (297) are functions of the spatial variable $\mathbf{x} \in \mathcal{B}$, and time $t \in \mathcal{T}$. They must satisfy field equations which follow from partial balance equations by a linear closure.

The partial balance equations appropriate for the chosen model are as follows

- mass conservation laws

$$\frac{\partial \rho^S}{\partial t} + \rho_0^S \operatorname{div} \mathbf{v}^S = 0, \quad \frac{\partial \rho^F}{\partial t} + \rho_0^F \operatorname{div} \mathbf{v}^F = 0, \quad (300)$$

- momentum balance equations

$$\rho_0^S \frac{\partial \mathbf{v}^S}{\partial t} = \operatorname{div} \mathbf{T}^S + \hat{\mathbf{p}}, \quad \rho_0^F \frac{\partial \mathbf{v}^F}{\partial t} = \operatorname{div} \mathbf{T}^F - \hat{\mathbf{p}}, \quad (301)$$

- balance equation of porosity

$$\frac{\partial (n - n_E)}{\partial t} + \operatorname{div} \mathbf{J} = \hat{n}, \quad (302)$$

- integrability condition for the deformation tensor

$$\frac{\partial \mathbf{e}^S}{\partial t} = \operatorname{sym} \operatorname{grad} \mathbf{v}^S. \quad (303)$$

This condition is related to the existence of a displacement vector \mathbf{u}^S . In the linear model such a vector leads to relations

$$\mathbf{v}^S = \frac{\partial \mathbf{u}^S}{\partial t}, \quad \mathbf{e}^S = \operatorname{sym} \operatorname{grad} \mathbf{u}^S.$$

Then the relation (303) becomes the identity. If we do not introduce the displacement vector, which is convenient in the wave analysis, then the relation (303) becomes the part of the set of field equations.

The partial stress tensors satisfy the following constitutive relations

$$\begin{aligned} \mathbf{T}'^S &= \mathbf{T}_0^S + \lambda^S e \mathbf{1} + 2\mu^S \mathbf{e}^S + Q\varepsilon \mathbf{1} + \beta(n - n_E) \mathbf{1}, \quad e := \operatorname{tr} \mathbf{e}^S, \\ \mathbf{T}'^F &= -p'^F \mathbf{1}, \quad p'^F = p_0^F - (\rho_0^F \kappa \varepsilon + Qe) + \beta(n - n_E), \\ n_E &= n_0 (1 + \delta e), \end{aligned} \quad (304)$$

where n_E denotes values of the porosity in the thermodynamical equilibrium which corresponds to vanishing sources $\hat{\mathbf{p}}, \hat{n}$. The constant tensor \mathbf{T}_0^S is the initial partial stress in the skeleton, p_0^F – the initial partial pressure in the fluid, and these quantities as well as the material parameters $\lambda^S, \mu^S, \kappa, Q, \delta, \beta$ are functions of an initial porosity n_0 . Certainly the parameters λ^S, μ^S correspond to classical Lamé constants while κ corresponds to the classical compressibility coefficient of an ideal fluid. The contribution with the parameter β is related to nonequilibrium changes of porosity and it may have an important bearing in the theory of nonlinear waves. It can be shown that it yields small contributions to volume changes of both components. We account for its presence only in the first part of our considerations.

The prime is used in the above relations to indicate a form of constitutive relations which follows directly by the linearization of the full nonlinear thermodynamical model. These relations shall be modified in the sequel.

The linear constitutive relations for the flux of porosity and for the sources have the following form

$$\mathbf{J} = \Phi_0 (\mathbf{v}^F - \mathbf{v}^S), \quad \hat{\mathbf{p}} = \pi (\mathbf{v}^F - \mathbf{v}^S) - N \text{grad } n, \quad \hat{n} = -\frac{n - n_E}{\tau}, \quad (305)$$

In the linear model the material parameters Φ_0, π, N, τ are constants depending solely on the initial porosity n_0 . Due to this property the contribution of the gradient of porosity can be incorporated into the partial stresses. Namely if we define modified constitutive relations by

$$\mathbf{T}^S := \mathbf{T}'^S - N(n - n_0) \mathbf{1}, \quad \mathbf{T}^F := \mathbf{T}'^F + N(n - n_0) \mathbf{1}, \quad (306)$$

then the source in the equations (301) contains solely the contribution of the diffusive force $\pi (\mathbf{v}^F - \mathbf{v}^S)$.

It is easy to see that the mass density ρ^S can be eliminated from the set of fields by integration of the mass balance equation (300)₁. According to (303) we have

$$\frac{\partial e}{\partial t} = \text{div } \mathbf{v}^S \quad \Rightarrow \quad \frac{\partial \rho^S}{\partial t} = -\rho_0^S \frac{\partial e}{\partial t} \quad \Rightarrow \quad e = \frac{\rho_0^S - \rho^S}{\rho_0^S}. \quad (307)$$

Simultaneously we can solve the porosity balance equation. We have

$$\frac{\partial(n - n_E)}{\partial t} + \frac{n - n_E}{\tau} = \Phi_0 \frac{\partial(e - \varepsilon)}{\partial t}. \quad (308)$$

Hence

$$n = n_0 \left[1 + \delta e + \frac{\Phi_0}{n_0} (e - \varepsilon) - \frac{\Phi_0}{n_0 \tau} \int_0^t (e - \varepsilon)|_{t-s} e^{-s/\tau} ds \right]. \quad (309)$$

The last contribution describes *memory effects* which are similar to these caused by the viscosity. In the first approximation they can be neglected in models describing acoustic waves in soils which corresponds to the assumption $\tau \rightarrow \infty$. We shall rely on this assumption in this Section.

Summing up the above considerations we see that the *full linear thermodynamical model without memory effects* contains the following essential fields

$$\{\mathbf{v}^S, \mathbf{v}^F, \mathbf{e}^S, \varepsilon\}, \quad (310)$$

which have to satisfy the field equations

$$\begin{aligned} \rho_0^S \frac{\partial \mathbf{v}^S}{\partial t} &= \text{div} \{ \lambda^S e \mathbf{1} + 2\mu^S \mathbf{e}^S + Q\varepsilon \mathbf{1} + \beta(n - n_E) \mathbf{1} - N(n - n_0) \mathbf{1} \} + \\ &\quad + \pi (\mathbf{v}^F - \mathbf{v}^S), \\ \rho_0^F \frac{\partial \mathbf{v}^F}{\partial t} &= -\text{grad} \{ -(\rho_0^F \kappa \varepsilon + Qe) + \beta(n - n_E) - N(n - n_0) \} - \\ &\quad - \pi (\mathbf{v}^F - \mathbf{v}^S), \end{aligned} \quad (311)$$

and

$$\begin{aligned}\frac{\partial \mathbf{e}^S}{\partial t} &= \text{sym grad } \mathbf{v}^S, \quad \frac{\partial \varepsilon}{\partial t} = \text{div } \mathbf{v}^F, \quad e \equiv \text{tr } \mathbf{e}^S, \\ n &= n_0 \left(1 + \delta e + \frac{\Phi_0}{n_0} (e - \varepsilon) \right).\end{aligned}\tag{312}$$

If we assume $\beta \equiv 0, N \equiv 0$, then the set of equations (311) coincides with the set of Biot's equations in which the coupling through the added mass was neglected. The classical Biot's model does not contain any counterpart of the relation (312)₄ for porosity. In soil mechanics one uses a kind of hybrid extension of Biot's model in order to specify n^3 . Results are identical with those following from (312) provided the parameters δ, Φ_0 are given by the relations (326) which we derive by means of the micro-macro transition.

We proceed to investigate relations between the above introduced macroscopic material parameters and real properties of materials constituting the porous medium.

9.3 Spherical static deformations

Description of granular materials by means of a macroscopic model is particularly easy when a deformation is homogeneous, spherically symmetric and the mechanical reactions of the system reduce to pressures. We consider such a system in this section in order to construct a simple micro-macro transition procedure for identification of some macroscopic material parameters.

In our notation we have for such a deformation

$$\mathbf{e}^S = \frac{1}{3} e \mathbf{1}, \quad p^S = -\frac{1}{3} \text{tr } \mathbf{T}^S, \quad p^F = -\frac{1}{3} \text{tr } \mathbf{T}^F,\tag{313}$$

and the *macroscopic constitutive relations* for partial pressures are as follows

$$p^S - p_0^S = -\left(\lambda^S + \frac{2}{3}\mu^S - n_0\beta\delta\right)e - Q\varepsilon + (N - \beta)(n - n_0),\tag{314}$$

$$p^F - p_0^F = -\rho_0^F \kappa \varepsilon - (Q + n_0\beta\delta)e - (N - \beta)(n - n_0).$$

Here we have already eliminated the equilibrium porosity $n_E = n_0(1 + \delta e)$.

In the static case the full pressure change must be in *equilibrium* with a given excess pressure Δp , i.e.

$$\Delta p = (p^S - p_0^S) + (p^F - p_0^F).\tag{315}$$

Clearly the problem to find volume changes e, ε , partial pressures p^S, p^F , and porosity n cannot be solved yet even if we account for the relation for porosity (312)₄. We have only 4 equations at the disposal and we need an additional equation specifying, for instance, a flow of the fluid through the boundary of the medium provided the problem remains homogeneous. This is natural for a two-component system and we present such equations in the sequel.

³assuming that the partial fluid mass density ρ^F , and the true fluid mass density ρ^{FR} are given one can calculate the porosity from the relation $n = \rho^F / \rho^{FR}$. However such a statement is useful under the assumption of incompressibility of the real fluid: $\rho^{FR} = \text{const.}$ A similar statement can be formulated under the incompressibility assumption of skeleton. Both of them are useless in acoustics.

However we proceed with the closure of the above problem in a different way. Namely we specify properties of the microstructure and relations between microscopic and macroscopic models. Then the problem can be solved and additional equations mentioned above serve solely the purpose of relating microscopic and macroscopic properties (compatibility conditions!). Such an approach is possible for static problems due to the homogeneity. Then solutions of partial momentum equations are trivial and the problem becomes algebraic.

The microscopic model for spherical deformations is specified as follows. Volume changes on this microscopic level are denoted by e^R, ε^R . Then e^R describes relative true volume changes of grains, and ε^R describes changes of the true mass density of the fluid in channels of the granular material. The corresponding pressures are denoted by p^{SR}, p^{FR} and, of course, the latter is identical with the pore pressure p_f . For these quantities the following *microscopic constitutive relations* are assumed

$$p^{SR} - p_0^{SR} = -K_s e^R, \quad p^{FR} - p_0^{FR} = -K_f \varepsilon^R. \quad (316)$$

In these relations K_s, K_f denote real (true) compressibility moduli of the solid component (granulae) and of the fluid, respectively. In contrast to material parameters of the macroscopic model, these can be measured independently of a current morphology of the granular material. They are not influenced by a porosity, cohesivity, or any other property characteristic for the texture of the medium.

The above presented macroscopic and microscopic properties are related through two sets of compatibility conditions.

On the one hand we have *dynamic compatibility relations* which for pressures have the form

$$p^S = (1 - n) p^{SR}, \quad p^F = n p^{FR}, \quad (317)$$

where n denotes the current porosity of the medium. On a boundary of the porous material we require the following equivalence of local partial stress tractions

$$\mathbf{T}^S \mathbf{n} dA = \mathbf{T}^{SR} \mathbf{n} dA^S, \quad \mathbf{T}^F \mathbf{n} dA = \mathbf{T}^{FR} \mathbf{n} dA^F, \quad (318)$$

where $\mathbf{T}^{SR}, \mathbf{T}^{FR}$ denote true partial stresses in the skeleton and in the fluid, respectively, \mathbf{n} is the unit outward normal to the surface, dA is an infinitesimal area of the surface, and dA^S, dA^F are contributions of the skeleton and of the fluid to this area: $dA = dA^S + dA^F$. If the surface fractions and volume fractions are the same, which follows under the assumption of randomness of the microstructure, we have $dA^S/dA = 1 - n, dA^F/dA = n$. Then (317) follows from (318) if the partial stresses reduce to pressures.

On the other hand we have the following relations between partial mass densities

$$\begin{aligned} \rho^S(\mathbf{x}, t) &= \frac{1}{V} \int_{REV(\mathbf{x}, t)} \rho^{SR}(\mathbf{z}, t) H^S(\mathbf{z}, t) dV_{\mathbf{z}}, \\ \rho^F(\mathbf{x}, t) &= \frac{1}{V} \int_{REV(\mathbf{x}, t)} \rho^{FR}(\mathbf{z}, t) H^F(\mathbf{z}, t) dV_{\mathbf{z}}, \end{aligned} \quad (319)$$

where $REV(\mathbf{x}, t)$ is the representative elementary volume located in the point \mathbf{x} of the macroscopic continuum at the time t , V denotes its volume, H^S is the characteristic function of the microstructural skeleton, i.e. it is equal to 1 when the point is occupied

by the solid and zero otherwise, and similarly for the characteristic function of the fluid $H^F = 1 - H^S$. If the microstructure is **homogeneous** we can write these relations in the form

$$\begin{aligned}\rho^S &= (1 - n) \rho^{SR}, \quad \rho^F = n \rho^{FR}, \\ n &= \frac{1}{V} \int_{REV(\mathbf{x}, t)} H^F(\mathbf{z}, t) dV_z \equiv 1 - \frac{1}{V} \int_{REV(\mathbf{x}, t)} H^S(\mathbf{z}, t) dV_z.\end{aligned}\quad (320)$$

Relating changes of mass densities to volume changes introduced earlier we obtain

$$\begin{aligned}\rho^S &= \rho_0^S (1 + e)^{-1}, \quad \rho^F = \rho_0^F (1 + \varepsilon)^{-1}, \\ \rho^{SR} &= \rho_0^{SR} (1 + e^R)^{-1}, \quad \rho^{FR} = \rho_0^{FR} (1 + \varepsilon^R)^{-1}.\end{aligned}\quad (321)$$

Through the combination of these relations and linearization we arrive immediately at the following *geometrical compatibility relations*

$$e = e^R + \frac{n - n_0}{1 - n_0}, \quad \varepsilon = \varepsilon^R - \frac{n - n_0}{n_0}.\quad (322)$$

Consequently for the 9 unknown quantities of spherical homogeneous deformations

$$\{e, \varepsilon, p^S, p^F, e^R, \varepsilon^R, p^{SR}, p^{FR}, n\},\quad (323)$$

we have 9 equations at the disposal: 1 equilibrium condition (315), 2 macroscopic constitutive relations (314), 2 microscopic constitutive relations (316), 2 dynamical compatibility relations (317), and 2 geometrical compatibility conditions (322). This simple algebraic problem can be solved.

As an intermediate result we obtain the following relations between geometrical microscopic quantities n, e^R and ε^R and macroscopic geometrical quantities e, ε

$$\begin{aligned}n - n_0 &= -\frac{1}{K_s - K_f} \left\{ [(\lambda^S + \frac{2}{3}\mu^S + Q) - (1 - n_0) K_s] e + \right. \\ &\quad \left. + [(Q + \rho_0^F \kappa) - n_0 K_f] \varepsilon \right\},\end{aligned}\quad (324)$$

$$\begin{aligned}e^R &= \frac{1}{(K_s - K_f)(1 - n_0)} \left\{ [(\lambda^S + \frac{2}{3}\mu^S + Q) - (1 - n_0) K_f] e + \right. \\ &\quad \left. + [(Q + \rho_0^F \kappa) - n_0 K_f] \varepsilon \right\},\end{aligned}$$

$$\begin{aligned}\varepsilon^R &= -\frac{1}{(K_s - K_f)n_0} \left\{ [(\lambda^S + \frac{2}{3}\mu^S + Q) - (1 - n_0) K_s] e + \right. \\ &\quad \left. + [(Q + \rho_0^F \kappa) - n_0 K_s] \varepsilon \right\}.\end{aligned}\quad (325)$$

Consequently, comparing (324) and (312) we see that the material parameters δ, Φ_0 , appearing in the relation for porosity can be expressed in terms of the other material parameters. We obtain

$$\delta = \frac{K_V - K}{n_0(K_s - K_f)}, \quad \Phi_0 = \frac{(Q + \rho_0^F \kappa) - n_0 K_f}{K_s - K_f},\quad (326)$$

$$K := \lambda^S + \frac{2}{3}\mu^S + \rho_0^F \kappa + 2Q, \quad K_V := (1 - n_0) K_s + n_0 K_f. \quad (327)$$

The material parameter K denotes the bulk compressibility modulus and K_V is the Voigt compressibility modulus.

Now, for the determination of e and ε we have the following two equations. The dynamical compatibility conditions (317) yield the following relation between the macroscopic volume changes

$$\begin{aligned} & \left\{ Q + \frac{K_f - N}{K_s - K_f} [(\lambda^S + \frac{2}{3}\mu^S + Q) - (1 - n_0) K_s] - \beta \frac{(Q + \rho_0^F \kappa) - n_0 K_f}{K_s - K_f} \right\} e = \\ & = - \left\{ [\rho_0^F \kappa - n_0 K_f] + \frac{K_f - N}{K_s - K_f} [(Q + \rho_0^F \kappa) - n_0 K_s] + \beta \frac{(Q + \rho_0^F \kappa) - n_0 K_f}{K_s - K_f} \right\} \varepsilon. \end{aligned} \quad (328)$$

Simultaneously the equilibrium condition (315) yields

$$\Delta p = - (\lambda^S + \frac{2}{3}\mu^S + Q) e - (\rho_0^F \kappa + Q) \varepsilon. \quad (329)$$

Hence substitution of ε calculated from (328) in (329) leads to e given in terms of the excess pressure Δp and, by means of (328), (325), (324), this determines in turn $\varepsilon, e^R, \varepsilon^R, n$ in terms of the excess pressure. Consequently, the constitutive relations give rise to partial pressures in terms of the excess pressure. This completes the solution of the problem. We shall not quote these simple results in this work due to their lengthy form.

In the next Subsection we present various forms of an additional equation which we have mentioned at the beginning of this Subsection.

In the Biot model it is customary to use a different field replacing the macroscopic volume change of the fluid ε . This variable, ζ , is called the increment of the fluid content. Its presence is related to the fact that, in contrast to the solid component, the representative elementary volume is not material for the fluid component. It means that REV consists always of the same particles of the real skeleton but the fluid may open and leave this domain due to the diffusion. The instantaneous mass of the fluid per macroscopic volume dV_0 is given by $\rho^F (1 + e) dV_0$ because e is the macroscopic measure of volume changes. Simultaneously in the same volume material with respect to the skeleton the initial amount of fluid mass was $\rho_0^F dV_0$. Consequently the change of the fluid mass contained in this volume is given by the difference of these two quantities. We introduce the dimensionless measure of this quantity

$$\zeta := \frac{1}{\rho_0^F} [(1 + e) \rho^F - \rho_0^F] \approx n_0 (e - \varepsilon). \quad (330)$$

This is the *increment of the fluid content*. We refer to this variable frequently in the further considerations. However it is clear that the transformation $(e, \varepsilon) \rightarrow (e, \zeta)$ is smooth and one-to-one and it can be done whenever convenient.

As mentioned before we neglect further the influence of nonequilibrium changes of porosity described in constitutive relations by the material parameter β . A justification of this simplification is based on the analysis of linear acoustic waves and it seems to be

indeed well found for soils. This parameter cannot be found by means of simple static experiments anyway.

Let us rewrite basic constitutive relations for spherical deformations (314) and the intermediate results (324), (325) using the material parameters introduced by Biot (e.g. see [41]). We have

$$\beta \equiv 0 \quad \Rightarrow$$

$$p - p_0 := (p^S - p_0^S) + (p^F - p_0^F) = -(K - n_0 C) e - n_0 C \varepsilon \equiv -K e + C \zeta,$$

$$\begin{aligned} p^{FR} - p_0^{FR} &\equiv p_f - p_f^0 := \frac{1}{n_0} (p^F - p_0^F) = -n_0 M \varepsilon - (C - n_0 M) e - N \frac{n - n_0}{n_0} \equiv \\ &\equiv M \zeta - C e - N \frac{n - n_0}{n_0}, \end{aligned}$$

$$\begin{aligned} n - n_0 &= -\frac{1}{K_s - K_f} \{[(K - n_0 C) - (1 - n_0) K_s] e + n_0 [C - K_f] \varepsilon\} \equiv \quad (331) \\ &\equiv -\frac{1}{K_s - K_f} \{[K - K_V] e - [C - K_f] \zeta\}, \end{aligned}$$

$$\begin{aligned} e^R &= \frac{1}{(K_s - K_f)(1 - n_0)} \{[(K - n_0 C) - (1 - n_0) K_f] e + n_0 [C - K_f] \varepsilon\} \equiv \\ &\equiv \frac{1}{(K_s - K_f)(1 - n_0)} \{[K - K_f] e - [C - K_f] \zeta\}, \end{aligned}$$

$$\begin{aligned} \varepsilon^R &= -\frac{1}{(K_s - K_f) n_0} \{[(K - n_0 C) - (1 - n_0) K_s] e + n_0 [C - K_s] \varepsilon\} \equiv \\ &\equiv -\frac{1}{(K_s - K_f) n_0} \{[K - K_s] e - [C - K_s] \zeta\}, \end{aligned}$$

where K, K_V are defined by (327) and in addition

$$C := \frac{1}{n_0} (Q + \rho_0^F \kappa), \quad M := \frac{\rho_0^F \kappa}{n_0^2}. \quad (332)$$

This notation simplifies the comparison of the present results with those appearing in the literature on soil mechanics.

Making use of the relations (331) and (316)₂ for the pore pressure $p_f - p_f^0 \equiv p^{FR} - p_0^{FR}$ we obtain immediately the relation between volume changes e and increments of fluid content ζ

$$\begin{aligned} &\left\{ C + \frac{K_f(K - K_s)}{n_0(K_s - K_f)} - \frac{N(K - K_V)}{n_0(K_s - K_f)} \right\} - \\ &- \left\{ M + \frac{K_f(C - K_s)}{n_0(K_s - K_f)} - \frac{N(C - K_f)}{n_0(K_s - K_f)} \right\} \frac{\zeta}{e} = 0, \end{aligned} \quad (333)$$

which must hold for all spherical static deformations.

9.4 Gedankenexperiments for compressibilities

9.4.1 Jacketed andunjacketed tests

As we have indicated earlier the macroscopic deformation problem of a two-component medium requires an additional boundary condition. In the case of static, homogeneous, spherically symmetric problems such a condition can be easily formulated. In Figure 2 we show schematically three simple tests considered commonly in soil mechanics which shall be considered in details.

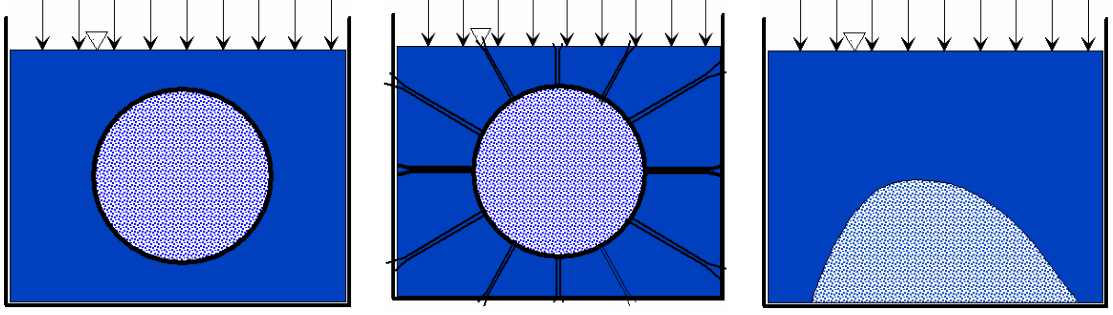


Figure 2: *Schemes of Gedankenexperiments: 1) jacketed undrained, 2) jacketed drained, 3) unjacketed.*

The additional conditions for those tests are as follows

- 1) jacketed undrained test in which the boundary of the sample is impermeable

$$\zeta = 0 \quad \Rightarrow \quad e = \varepsilon; \quad (334)$$

it means that there is no flow through the boundary and, consequently, macroscopic volume changes of both components must be equal,

- 2) jacketed drained test in which there is a drainage of the sample connecting the fluid component directly with the external world; then

$$p^{FR} = p_0^{FR} \quad \Rightarrow \quad \varepsilon^R = 0; \quad (335)$$

- 3) unjacketed test in which the pore pressure and the external fluid pressure must be the same, i.e.

$$p^{FR} - p_0^{FR} = \Delta p, \quad (336)$$

where Δp is a given excess pressure.

These tests are called Gedankenexperiments because they can be principally performed under ideal conditions (e.g. when capillary effects, viscosity, temperature changes etc. can be neglected), and, simultaneously, they lead to relations between physical properties – in our case, between macroscopic and microscopic material parameters.

Such procedures were proposed often for materials with microstructure. For instance, macroscopic properties of polycrystals were calculated by means of properties of grains

by W. Voigt [48] (consistent stresses), A. Reuss [40] (consistent strains) or by means of some fully consistent micro-macro transition procedures, properties of composites were calculated by means of some homogenization procedures, etc. The above described simple tests appear in the literature on granular materials in a more or less explicit form since the works of F. Gassmann [21], J. Geertsma [22], M. A. Biot and D. G. Willis [13], and many others. The problem is still investigated and we refer to modern review works of J. E. White [50], R. D. Stoll [41], or J. G. Berryman [11] who present also various applications of the results of such an analysis.

The approach presented in this work differs from the previous presentations because the model contains an additional material parameter N . Simultaneously this systematic approach to the micro-macro transition enables generalizations to such systems in which we cannot assume full saturation or neglect capillary or viscous effects.

The **jacketed undrained** test described by (334) yields immediately the *first compatibility relation* between material parameters

$$\mathcal{C}_1 := C + \frac{K_f(K - K_s) - N(K - K_V)}{n_0(K_s - K_f)} = 0. \quad (337)$$

We proceed to investigate the **jacketed drained** test.

It is commonly assumed that in addition to microscopic tests which deliver compressibilities K_s, K_f one can measure the so-called *drained compressibility modulus* K_d . This is defined as the negative fraction of the excess pressure Δp to the macroscopic volume change e in the drained jacketed test. Hence we have for $\beta \equiv 0$

$$\begin{aligned} K_d &: = -\frac{\Delta p}{e} = -\frac{(p^S - p_0^S) + (p^F - p_0^F)}{e} = \\ &= -\frac{1}{e} \{-(K - n_0 C)e - n_0 C \varepsilon\} \equiv K - C \frac{\zeta}{e}. \end{aligned} \quad (338)$$

We can eliminate the fraction $\frac{\zeta}{e}$ either by means of the macroscopic condition for pore pressure (335)₁ or by means of the microscopic condition on volume changes of the fluid (335)₂. Bearing the relation (331)₂ in mind we obtain in the first case the following *second compatibility relation* between material parameters

$$\mathcal{C}_2 := n_0 - \frac{C}{M} - \frac{K_b}{K_s} \frac{1 - (1 - n_0) \frac{K_s}{K_b}}{1 - \frac{1 - n_0}{n_0} \frac{NC}{K_b M}} \left\{ 1 - \frac{N(K - n_0 C)}{n_0 M K_b} \right\} = 0, \quad (339)$$

$$K_b := K - \frac{C^2}{M},$$

where we have used the relation (331)₃ for the porosity.

In the second case we substitute (331)₅ for ε^R and obtain the *third compatibility relation* between material parameters

$$\mathcal{C}_3 := K - K_d - C \frac{C - N}{M - \frac{N}{n_0}} = 0. \quad (340)$$

Finally, for the **unjacketed** test, we have due to the equilibrium condition (315) the equality of the full pressure given by (331)₁ and the pore pressure (316)₂. This yields the *fourth compatibility relation* between material parameters

$$\begin{aligned} \mathcal{C}_4 := & \left(1 - \frac{K}{K_W}\right) \left(M - C - N \frac{1-n_0}{n_0} \frac{C}{K_s}\right) + \\ & + \left(1 - \frac{C}{K_W}\right) \left(K - C - N \frac{1-n_0}{n_0} \left(1 - \frac{K}{K_s}\right)\right) = 0, \quad \frac{1}{K_W} := \frac{1-n_0}{K_s} + \frac{n_0}{K_f}. \end{aligned} \quad (341)$$

The set of relations

$$\{\mathcal{C}_1, \mathcal{C}_2, \mathcal{C}_3, \mathcal{C}_4\} = 0 \quad (342)$$

forms four equations for four material parameters $\{K, C, M, N\}$, or equivalently for $\{\lambda^S + \frac{2}{3}\mu^S, \kappa, Q, N\}$ in terms of the material parameters $\{K_s, K_f, K_d\}$ and the initial porosity n_0 . It is nonlinear and, consequently, possesses more than one solution. As it cannot be solved analytically we present further some typical numerical results. For data used in the example there exist two physically reasonable solutions in which all four quantities K, M, C, N are real and nonnegative.

However one analytical solution can be constructed in the fully general case. Namely, substitution of the parameter $N = 0$ in $\{\mathcal{C}_1, \mathcal{C}_3, \mathcal{C}_4\} = 0$ yields the following set of equations

$$\begin{aligned} K - K_s + n_0 C \frac{K_s - K_f}{K_f} &= 0, \quad K_d - K + \frac{C^2}{M} = 0, \\ K \left(1 - \frac{C}{K}\right) - C + M - \frac{MK_d}{K_W} &= 0. \end{aligned} \quad (343)$$

We see further that this set possesses two real positive solutions. One of them can be found analytically and it has the form

$$K = \frac{(K_s - K_d)^2}{\frac{K_s^2}{K_W} - K_d} + K_d, \quad C = \frac{K_s (K_s - K_d)}{\frac{K_s^2}{K_W} - K_d}, \quad M = \frac{K_s^2}{\frac{K_s^2}{K_W} - K_d}. \quad (344)$$

These are the famous *Gassmann relations* appearing in Biot's model (e.g. [41]). It is rather amazing that they satisfy **identically** the equation $\mathcal{C}_2 = 0$ with $N = 0$. Consequently $\{K, C, M\}$ given by (344) and $N = 0$ constitute a solution of the full system of compatibility conditions. It yields the important conclusion that

Biot's model whose material parameters satisfy the above Gassmann relations is thermodynamically admissible in spite of the fact that its constitutive relations for partial stresses do not contain a dependence on the porosity gradient.

This property follows solely for the linear model in which the contribution of the porosity gradient can be incorporated in constitutive relations for stresses.

Let us note in passing that in the usual derivation of Gassmann relations the compatibility of these relations with the jacketed drained test is ignored – this test is solely used as a motivation of the definition of the drained compressibility modulus K_d – and, in

addition, it is assumed that the porosity in theunjacketed experiment is constant. Details can be found, for instance, in the book of Stoll [41]. Substitution of Gassmann relations in the formula (331) for changes of porosity shows that $n = n_0$, i.e. the porosity follows as a constant in this experiment and does not have to be assumed to be constant as claimed by Stoll.

Let us comment on the condition $\mathcal{C}_2 = 0$. This condition is violated by the second solution of the set (343). We demonstrate it in the next Subsection on a numerical example. However this solution can be used as a first step of an iteration procedure for calculating a solution with $N \neq 0$. It is essential in the full model with an additional contribution of the porosity gradient. If the parameter N is small in comparison with other material parameters of the model we can iterate the solution of the full set $\{\mathcal{C}_1, \mathcal{C}_2, \mathcal{C}_3, \mathcal{C}_4\} = 0$ assuming that the second solution of Gassmann equations forms a zeroth step of iteration and $\mathcal{C}_2 = 0$ serves the purpose of determining N in this iteration level. Then we can proceed to the second step of iteration and so on. It is easy to show that such a procedure indeed converges to the full solution of the system. We shall not pursue any theoretical analysis of this method in this work and present rather a numerical example.

9.4.2 A numerical example

As mentioned above the set of equations $\{\mathcal{C}_1, \mathcal{C}_2, \mathcal{C}_3, \mathcal{C}_4\} = 0$ for material parameters $\{K, M, C, N\}$ cannot be solved analytically. However, it is a rather simple algebraic system which can be handled numerically with any standard package. Below we show such numerical results calculated by means of the package MAPLE 7.0. We have chosen the following data for these calculations

$$K_s = 48 \times 10^9 Pa, \quad K_f = 2.25 \times 10^9 Pa, \quad K_d = \frac{K_s}{1 + gn_0}, \quad (345)$$

where the last empirical relation is proposed after Geertsma (e.g. see: [50] where it is claimed that $g = 50$ gives a good fit with experimental data for many soils). We choose the values $g = 30$ and 50 for the illustration of Gassmann equations and solely $g = 50$ for the full model.

In Figures 3 and 4 we show numerical solutions of Gassmann equations (343). Solution 2 (denoted as sol.2 in Figures) satisfies relations (344) and, simultaneously, the equation $\mathcal{C}_2 = 0$ with $N = 0$. Consequently, this solution is also a solution of the full general set of compatibility relations. Solution 1 (denoted as sol.1 in Figures) in Figure 3 satisfies equations (343) but not the compatibility condition $\mathcal{C}_2 = 0$. Hence, it is not a solution of the full set and has no practical bearing. It is interesting to observe that solution 1 yields negative values of the coupling parameter Q for high values of porosity. This would yield instabilities (expansion under pressure). In addition to the violation of the compatibility relation this would eliminate an applicability of this solution.

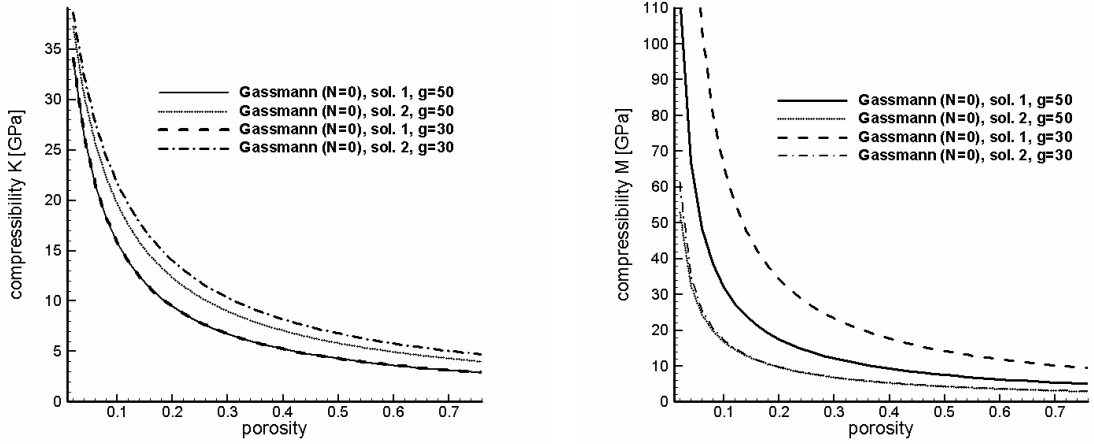


Figure 3: *Compressibility modulus K (left) and compressibility modulus M (right) according to Gassmann equations (343) for two values of Geertsma parameter $g = 30, 50$.*

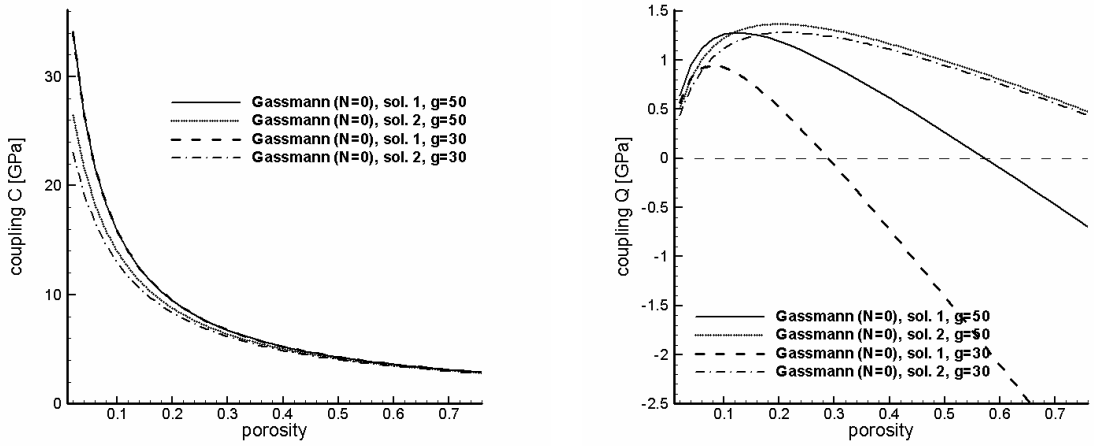


Figure 4: *Coupling parameters C (left) and Q (right) according to Gassmann equations (343) for two values of Geertsma parameter $g = 30, 50$.*

Let us make two observations essential for the further analysis. It is seen that the change of Geertsma parameter does not yield any qualitative changes in the behavior of the parameters. The model becomes stiffer for smaller values of g . For this reason we present further results for the full model choosing only one value of Geertsma parameter: $g = 50$. Secondly, it is seen in Figure 4 that values of the coupling parameter Q are much smaller than values of compressibility moduli K, M . This is an important conclusion for the construction of acoustics by means of the model without any coupling between stresses at all (e.g. [63], [59], [7]).

We proceed to the presentation of results for the full model. The set of compatibility relations has been solved by iteration with respect to the parameter N . It has been found that the iteration converges very fast for small values of porosity and it slows down with growing porosity until, at approximately $n_0 = 0.58$, the procedure is not convergent anymore. One would have to use a different iteration procedure in order to find solutions for higher values of porosity. This has not been done because such results would have no

physical bearing. Namely, for such values the coupling parameter Q becomes negative and this yields constitutive instability. Such an instability does not appear in Biot's model.

Let us inspect the numerical results. In Figure 5 we compare all material parameters K, M, C, N for the Biot model (left) and for the full model (right). Clearly $N = 0$ in the case of Biot's model. It is seen that there is a good qualitative agreement of both models and quantitatively both models agree quite well for porosities bigger than 0.2. It is essential to notice that the curves for C and N intersect each other for the full model at $n_0 \approx 0.58$. As we see further this appears in the point of loss of stability. At this point the iteration was terminated.

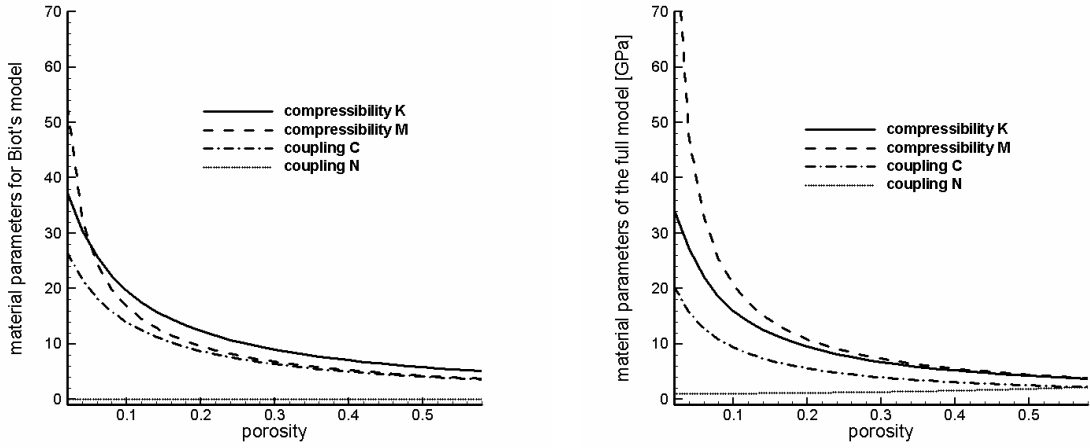


Figure 5: Comparison of material parameters for Biot's model (left) and the full model with the porosity gradient (right) with Geertsma parameter $g = 50$.

On the left hand side of Figure 6 we compare directly compressibilities K, M for both models. Obviously the compressibility modulus of the skeleton K is higher (app. 20%) for Biot's model than it is in the full model but it is the other way around for the compressibility of the fluid M .

The coupling coefficient Q agrees qualitatively for both models and for the porosity $n_0 < 0.58$ (Figure 6, right) but the quantitative differences are essential. This coupling is much stronger in Biot's model and it becomes negative in the full model for $n_0 \gtrsim 0.58$. It means, as we have already mentioned, that an increment of pressure would lead to an increment of volume (i.e. a nonconvex potential of stresses) which, according to classical arguments of continuum mechanics, yields an instability .

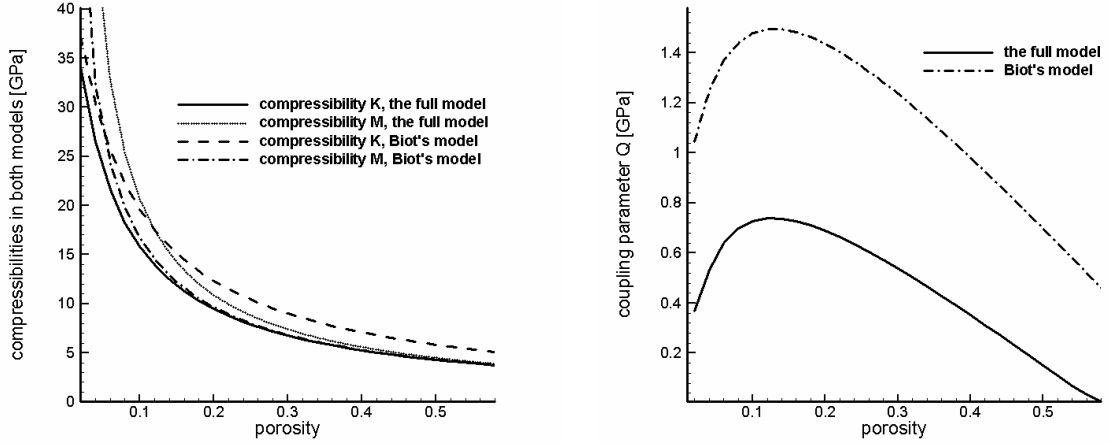


Figure 6: Comparison of the compressibilities K, M (left) and of the coupling parameter Q (right) for the full model and Biot's model with Geertsma parameter $g = 50$.

We proceed to present results for the coefficients δ and Φ_0 describing the behavior of the current porosity n (see: relation (312)₃). These are shown in Figure 7. It is clear that equilibrium changes of porosity proportional to volume changes of the skeleton e are much bigger than nonequilibrium changes proportional to the difference of volume changes $e - \varepsilon$ (i.e. to the increment of fluid contents ζ). The parameter δ is app. 20 times bigger than the nonequilibrium parameter Φ_0/n_0 . Changes of porosity are apparently more significant in the range of small initial porosities than for large initial porosities.

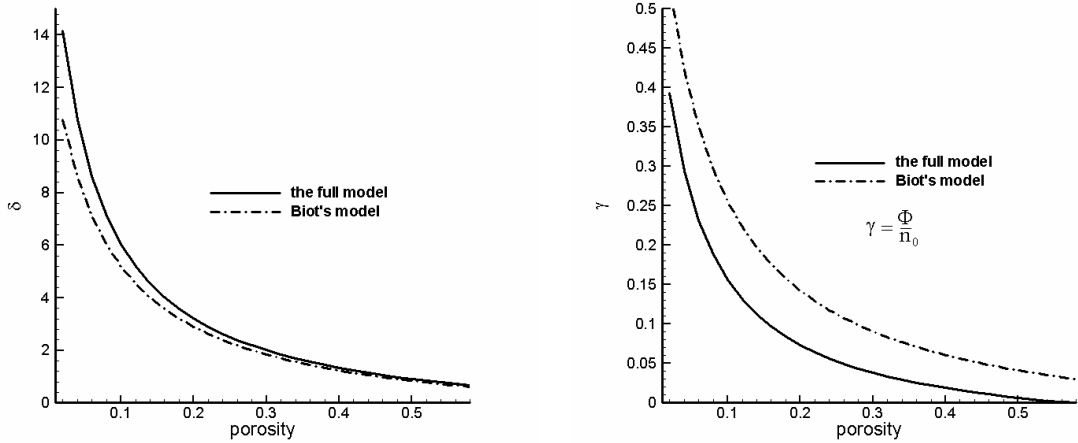


Figure 7: Coefficients of porosity relation: equilibrium part δ , and nonequilibrium part $\gamma = \Phi_0/n_0$ with Geertsma parameter $g = 50$.

9.5 Concluding remarks

The results presented in this Section demonstrate the position of the classical Biot model for linear poroelastic media among thermodynamically admissible models following as limit cases from a fully nonlinear model with a balance equation of porosity.

The most important conclusion of the above presented analysis of the micro-macro transition is that Biot's model follows as a special case of the full thermodynamical model in which the coupling with the porosity gradient vanishes ($N = 0$). Simultaneously the micro-macro transition yields compatibility relations which possess *two* solutions for material parameters. One of them coincides with classical Gassmann relations for Biot's model. The other yields a model in which the coupling with the porosity gradient is present. These two models seem to be possible due to the linearity assumption. The extension of the classical nonlinear two-component model of immiscible mixtures by adding a dependence on the porosity gradient is necessary for the existence of coupling between partial stresses and this dependence survives in nonlinear models not covered by the micro-macro transition applied in this work.

In order to obtain Biot's constitutive relations for stresses it is necessary as well to leave out relaxation properties of the porosity (memory effects) which may appear in the general thermodynamical model.

In the full thermodynamical model there appears a material instability for initial porosities higher than app. 0.58 – at least for the data used in the numerical analysis. This may be related to a real instability indicated by J. Dvorkin (e.g. [36]) which he assigns to the fluidization.

The numerical results presented in the previous Subsection show that in practically relevant cases of analysis of acoustic waves both couplings – Biot's coupling of stresses with the parameter Q as well as the coupling through the porosity gradient with the parameter N – can be neglected without any qualitative consequences and very little quantitative influence on propagation conditions. The last conclusion is presented more extensively in the work [7].

Moreover, at least for granular materials for which the above micro-macro transition analysis is better justified than for rocks, changes of porosity in the wave analysis of linear acoustic waves can be assumed to be caused solely by volume changes of the skeleton. An influence of the increment of fluid content on these changes is of the order of a few percent of this following volume changes of the skeleton.

10 Fundamentals of acoustic waves in linear poro-elastic media

Theory of propagation of acoustic waves is one of the main reasons of construction of poroelastic models. In many applications, particularly in geophysics, an assumption on the elastic, reversible, character of deformation cannot be made as real processes are irreversible and contain viscous, plastic deformations, damage, creation of cracks, etc. However, a dynamical disturbance of small amplitude may propagate without considerable irreversible changes of the material. For this reason, it can be used in *nondestructive testing*. This is indeed the most important application of the poroelastic models.

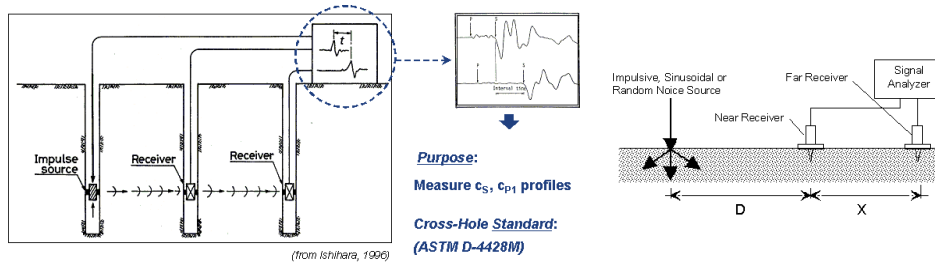


Figure 8: Schemes of wave tests in soil mechanics. The left panel: longitudinal waves, the right panel: surface waves.

In Figure 8, we show schematically the two most typical nondestructive tests performed in soils. As the result, one obtains speeds of propagation and attenuation of different waves and these are used for the determination of various parameters of the material. Waves are induced in these tests by an impuls created by a small explosion in the borehole, by a vibrator, by hammering on the plate, or by some other means controlled by the technician. However, one uses also natural sources of waves. The main source of data on the earth structure are earthquakes (of course, also atomic explosions!), and a geological structure on the depth of a few kilometers is investigated by means of measuring waves stemming from microearthquakes created by propagation of small cracks near boreholes.

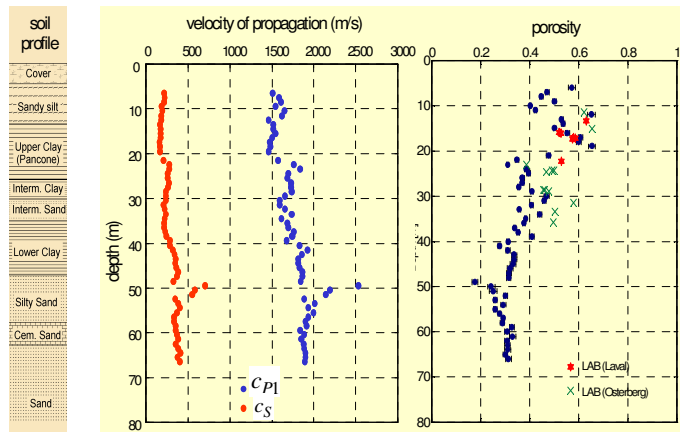


Figure 9: Speeds of propagation of longitudinal (c_{p1}) and transversal (c_s) and the resulting porosity in the vicinity of Pisa tower.

In Figure 9 we show a typical result of such a measurement (compare the article of Carlo Lai in [31]).

In this Section we present the main features of the theory of linear waves in poroelastic materials.

10.1 Wave front

Let us remind a few elementary properties of the description of wave fronts in continua. Acoustic waves in continua are related to the propagation of a nonmaterial singular surface – the *wave front* \mathcal{S} – on which acceleration fields are discontinuous but the velocity fields remain continuous. If the latter does not hold we deal with either shock waves or with vortex sheets.

Let us assume that the instantaneous geometry of the front \mathcal{S} is given by the following equation

$$f(\mathbf{x}, t) = 0, \quad \mathbf{x} \in \mathcal{B}_t \subset \mathbb{R}^3, \quad t \in \mathcal{T}, \quad (346)$$

which is at least of the class \mathcal{C}^2 with respect to \mathbf{x} , and of the class \mathcal{C}^1 with respect to time t . \mathcal{B}_t denotes the current configuration of the skeleton. The smoothness requirements mean that changes of the normal vector to the surface are differentiable, and changes of curvatures are continuous. Simultaneously there exists a smooth speed of propagation of the surface. In order to see these properties we use the identity

$$df \equiv d\mathbf{x} \cdot \text{grad } f + dt \frac{\partial f}{\partial t} = 0. \quad (347)$$

As the gradient of f is orthogonal to the surface (f is constant along the surface, i.e. the vector $\text{grad } f$ may possess solely an orthogonal component) we can define a unit normal vector by the relation

$$\mathbf{n} := \frac{\text{grad } f}{|\text{grad } f|}. \quad (348)$$

The second gradient of f , i.e. a quantity proportional to $\text{grad } \mathbf{n}$ is related to curvatures. Bearing the relation (347) in mind we obtain for the speed of propagation

$$c := \frac{d\mathbf{x}}{dt} \cdot \mathbf{n} = -\frac{\frac{\partial f}{\partial t}}{|\text{grad } f|}. \quad (349)$$

It is easy to see that the relation (346) does not impose any conditions on the tangential component of the velocity of the surface. This means that kinematics of slip motions cannot be described by such a relation. However this is immaterial in the theory of waves.

If the speed of propagation c is given then the relation (349) is the nonlinear differential equation for the function f

$$\frac{\partial f}{\partial t} + c |\text{grad } f| = 0. \quad (350)$$

With an appropriate initial condition for the position of the front (i.e. $f(\mathbf{x}, t = 0)$ – given) this equation forms a nonlinear Cauchy problem.

10.2 Propagation of fronts of acoustic waves in Biot's model and simple mixture model

We proceed to present an example of analysis of weak discontinuity (acoustic) waves for Biot's model as well as the "simple mixture" model in which both the coupling Q and the tortuosity coefficient $(a - 1)$ are assumed to be zero. Similarly to Biot's model the latter model has already a rather extensive literature (for the review of results, see: [59], [7]).

The main aim of this analysis is to show that differences between these two models are solely quantitative. This has a particular bearing in applications to such complex problems as the propagation of surface waves which play an important role in nondestructive testing of porous materials.

Let us repeat the set of equations of Biot's model (194), (195) with a small modification of the notation. For the fields $\mathbf{v}^S, \mathbf{v}^F, \mathbf{e}^S, \varepsilon$, we have the field equations

$$\rho_{11} \frac{\partial \mathbf{v}^S}{\partial t} + \rho_{12} \frac{\partial \mathbf{v}^F}{\partial t} = \lambda^S \text{grad tr } \mathbf{e}^S + 2\mu^S \text{div } \mathbf{e}^S + Q \text{grad } \varepsilon + \pi (\mathbf{v}^F - \mathbf{v}^S), \quad (351)$$

$$\rho_{22} \frac{\partial \mathbf{v}^F}{\partial t} + \rho_{12} \frac{\partial \mathbf{v}^S}{\partial t} = \kappa \rho_0^F \text{grad } \varepsilon + Q \text{grad tr } \mathbf{e}^S - \pi (\mathbf{v}^F - \mathbf{v}^S),$$

where

$$\begin{aligned} \frac{\partial \mathbf{e}^S}{\partial t} &= \text{sym grad } \mathbf{v}^S, \quad \frac{\partial \varepsilon}{\partial t} = \text{div } \mathbf{v}^F, \\ \rho_{11} &= \rho_0^S [1 - r(1 - a)], \quad \rho_{12} = r(1 - a) \rho_0^S, \quad \rho_{22} = r a \rho_0^S, \\ a &= \frac{1}{2} \left(\frac{1}{n_0} + 1 \right), \quad r = \frac{\rho_0^F}{\rho_0^S}. \end{aligned} \quad (352)$$

We begin the analysis of this system by proving its hyperbolicity. To this aim we consider the propagation of the front \mathcal{S} of the weak discontinuity wave, i.e. of a singular surface on which

$$[[\mathbf{v}^S]] = 0, \quad [[\mathbf{v}^F]] = 0, \quad (353)$$

where $[[\dots]]$ denotes the jump of the quantity. On such a surface the accelerations may be discontinuous and we call their jumps the **amplitudes of discontinuity**

$$\mathbf{a}^S := \left[\left[\frac{\partial \mathbf{v}^S}{\partial t} \right] \right], \quad \mathbf{a}^F := \left[\left[\frac{\partial \mathbf{v}^F}{\partial t} \right] \right]. \quad (354)$$

Then the following compatibility conditions hold⁴

$$[[\text{grad } \mathbf{v}^S]] = -\frac{1}{c} \mathbf{a}^S \otimes \mathbf{n}, \quad [[\text{grad } \mathbf{v}^F]] = -\frac{1}{c} \mathbf{a}^F \otimes \mathbf{n}, \quad (355)$$

⁴The behaviour of various kinematic quantities on singular surfaces has been studied since 150 years and the modern theory follows the way proposed by Hadamard. An excellent presentation of this subject can be found in the classical book of C. Truesdell and R. A. Toupin [46] (Chapter IV). We use further a particular case of these kinematic compatibility conditions following under the assumption of continuity of both motions and velocities.

$$[[\text{grad } \mathbf{e}^S]] = -\frac{1}{c} \left[\left[\frac{\partial \mathbf{e}^S}{\partial t} \right] \right] \otimes \mathbf{n}, \quad [[\text{grad } \varepsilon]] = -\frac{1}{c} \left[\left[\frac{\partial \varepsilon}{\partial t} \right] \right] \mathbf{n},$$

where c is the speed of propagation of the surface \mathcal{S} and \mathbf{n} its unit normal vector. The latter gives, of course, the direction of propagation of the wave.

Bearing (352) in mind we obtain immediately

$$\begin{aligned} [[\text{grad } \mathbf{e}^S]] &= \frac{1}{2c^2} (\mathbf{a}^S \otimes \mathbf{n} + \mathbf{n} \otimes \mathbf{a}^S) \otimes \mathbf{n}, \\ [[\text{grad } \varepsilon]] &= \frac{1}{c^2} \mathbf{a}^S \cdot \mathbf{n} \mathbf{n}. \end{aligned} \quad (356)$$

We evaluate the jump of field equations (351) on the surface \mathcal{S} . It follows immediately

$$\begin{aligned} [\rho_{11}c^2 \mathbf{1} - \lambda^S \mathbf{n} \otimes \mathbf{n} - \mu^S (\mathbf{1} + \mathbf{n} \otimes \mathbf{n})] \mathbf{a}^S + [\rho_{12}c^2 \mathbf{1} - Q \mathbf{n} \otimes \mathbf{n}] \mathbf{a}^F &= 0, \\ [\rho_{12}c^2 \mathbf{1} - Q \mathbf{n} \otimes \mathbf{n}] \mathbf{a}^S + [\rho_{22}c^2 \mathbf{1} - \kappa \rho_0^F \mathbf{n} \otimes \mathbf{n}] \mathbf{a}^F &= 0. \end{aligned} \quad (357)$$

This is clearly an eigenvalue problem. We say that the system (351) is **hyperbolic** if the eigenvalues c are real and the corresponding eigenvectors $[\mathbf{a}^S, \mathbf{a}^F]$ linearly independent. We prove that this is indeed the case.

It is convenient to separate the transversal and longitudinal parts of the problem (357). The **transversal** part follows if we take the scalar product of the equations with a vector \mathbf{n}_\perp perpendicular to \mathbf{n} . We obtain

$$\begin{aligned} (\rho_{11}c^2 - \mu^S) a_\perp^S + \rho_{12}c^2 a_\perp^F &= 0, \\ \rho_{12}a_\perp^S + \rho_{22}a_\perp^F &= 0, \\ a_\perp^S &:= \mathbf{a}^S \cdot \mathbf{n}_\perp, \quad a_\perp^F := \mathbf{a}^F \cdot \mathbf{n}_\perp. \end{aligned} \quad (358)$$

Hence we have for the speed of the front

$$c^2 = \frac{\rho_{22}}{\rho_{11}\rho_{22} - \rho_{12}^2} \mu^S. \quad (359)$$

As $\rho_{22} > 0$, $\mu^S > 0$ it follows the **first condition for hyperbolicity** of the set (351)

$$a - r(1 - a) > 0. \quad (360)$$

This condition is obviously fulfilled because a is not smaller than 1.

The speed of propagation (359) describes the shear wave. It is easy to see that in the particular case without the influence of tortuosity $a = 1$ this relation reduces to the classical formula

$$c = c_S = \sqrt{\mu^S / \rho_0^S} \quad (361)$$

In this case, according to (358)₂, the amplitude in the fluid a_\perp^F is zero, i.e. the shear wave is carried solely by the skeleton.

We proceed to the **longitudinal** part. To this aim we take the scalar product of the relations (357) with the vector \mathbf{n} . It follows

$$\begin{aligned} [\rho_{11}c^2 - (\lambda^S + 2\mu^S)] \mathbf{a}^S \cdot \mathbf{n} + [\rho_{12}c^2 - Q] \mathbf{a}^F \cdot \mathbf{n} &= 0, \\ [\rho_{12}c^2 - Q] \mathbf{a}^S \cdot \mathbf{n} + [\rho_{22}c^2 - \kappa \rho_0^F] \mathbf{a}^F \cdot \mathbf{n} &= 0, \end{aligned} \quad (362)$$

and the dispersion relation is as follows

$$r \left[(1 - r(1 - a)) c^2 - c_{P1}^2 \right] \left[a c^2 - c_{P2}^2 \right] - \left[r(1 - a) c^2 - \frac{Q}{\rho_0^S} \right]^2 = 0, \quad (363)$$

where

$$c_{P1}^2 := \frac{\lambda^S + 2\mu^S}{\rho_0^S}, \quad c_{P2}^2 := \kappa. \quad (364)$$

The eigenvalues of this problem have the form

$$c^2 = \frac{1}{2r[a - r(1 - a)]} \left[A \pm \sqrt{B} \right], \quad (365)$$

where

$$\begin{aligned} A &:= r a c_{P1}^2 + [1 - r(1 - a)] r c_{P2}^2 - 2 \frac{Q}{\rho_0^S} r(1 - a), \\ B &:= A^2 - 4r[a - r(1 - a)] \left[c_{P1}^2 c_{P2}^2 r - \frac{Q^2}{\rho_0^{S2}} \right]. \end{aligned} \quad (366)$$

It can be easily shown that under the condition (360) $B > 0$ for all $a \geq 1$, $Q \geq 0$. However, c^2 defined by (365) is positive solely if the additional condition on Q is satisfied

$$Q \leq \rho_0^S \sqrt{r c_{P1} c_{P2}} \equiv \sqrt{\rho_0^F \kappa (\lambda^S + 2\mu^S)}. \quad (367)$$

This is the **second condition for hyperbolicity**.

In the particular case $a = 1$, $Q = 0$ we have c equal to either c_{P1} or c_{P2} which means that the set is unconditionally hyperbolic.

The two solutions for c^2 define two longitudinal modes of propagation, P1 and P2. The P2-mode, called the Biot wave or the **slow wave** in the theory of porous materials, is also known as the **second sound** and it appears in all two-component systems described by hyperbolic field equations. For instance, it is known in the theory of binary mixtures of fluids in which it is applied to describe dynamical properties of liquid helium as discovered by L. Tisza in 1938 [42]. For porous materials, it has been discovered by Ya. Frenkel in 1944 [20].

10.3 Biot's model vs. the simple mixture model on the example of monochromatic acoustic waves

The above analysis yields solely the propagation properties of the wave front \mathcal{S} . We do not learn anything about, for instance, the attenuation of the waves. For this reason we proceed to analyze monochromatic waves. As we see the speeds of propagation obtained above follow in the limit of frequency $\omega \rightarrow \infty$.

We seek solutions of equations (351) which have the form of the following monochromatic waves

$$\mathbf{v}^S = \mathbf{V}^S \mathcal{E}, \quad \mathbf{v}^F = \mathbf{V}^F \mathcal{E}, \quad \mathbf{e}^S = \mathbf{E}^S \mathcal{E}, \quad \varepsilon = E^F \mathcal{E}, \quad (368)$$

$$\mathcal{E} := \exp [i (\mathbf{k} \cdot \mathbf{x} - \omega t)],$$

where $\mathbf{V}^S, \mathbf{V}^F, \mathbf{E}^S, E^F$ are constant amplitudes, \mathbf{k} is the wave vector, ω real frequency. This should be understood in the following way: the wave number, $k := \sqrt{\mathbf{k} \cdot \mathbf{k}} = \text{Re } k + i \text{Im } k$, is complex and the direction of propagation $\mathbf{n} := \mathbf{k}/k$ real which yields $\exp(i\mathbf{k} \cdot \mathbf{x}) = \exp(-\text{Im } k (\mathbf{n} \cdot \mathbf{x})) \exp[i(\text{Re } k (\mathbf{n} \cdot \mathbf{x}) - \omega t)]$, i.e. contributions of the attenuation and of the progressive wave.

Substitution of this ansatz in field equations yields the following compatibility conditions

$$\begin{aligned} & [\rho_{11}\omega^2 \mathbf{1} - \lambda^S \mathbf{k} \otimes \mathbf{k} - \mu^S (k^2 \mathbf{1} + \mathbf{k} \otimes \mathbf{k}) + i\pi\omega \mathbf{1}] \mathbf{V}^S + \\ & + [\rho_{12}\omega^2 \mathbf{1} - Q \mathbf{k} \otimes \mathbf{k} - i\pi\omega \mathbf{1}] \mathbf{V}^F = 0, \\ & [\rho_{12}\omega^2 \mathbf{1} - Q \mathbf{k} \otimes \mathbf{k} - i\pi\omega \mathbf{1}] \mathbf{V}^S + [\rho_{22}\omega^2 \mathbf{1} - \kappa \rho_0^F \mathbf{k} \otimes \mathbf{k} + i\pi\omega \mathbf{1}] \mathbf{V}^F = 0. \end{aligned} \quad (369)$$

As usual, the problem of existence of such waves reduces to the eigenvalue problem with the eigenvector $[\mathbf{V}^S, \mathbf{V}^F]$. As before we split the problem into two parts: in the direction \mathbf{k}_\perp perpendicular to \mathbf{k} (transversal modes) and in the direction of the wave vector \mathbf{k} (longitudinal modes).

For transversal modes (monochromatic shear waves) we have

$$\begin{aligned} & [\rho_{11}\omega^2 - \mu^S k^2 + i\pi\omega] V_\perp^S + [\rho_{12}\omega^2 - i\pi\omega] V_\perp^F = 0, \quad k^2 = \mathbf{k} \cdot \mathbf{k}, \\ & [\rho_{12}\omega^2 - i\pi\omega] V_\perp^S + [\rho_{22}\omega^2 + i\pi\omega] V_\perp^F = 0, \\ & V_\perp^S = \mathbf{V}^S \cdot \mathbf{k}_\perp, \quad V_\perp^F = \mathbf{V}^F \cdot \mathbf{k}_\perp. \end{aligned} \quad (370)$$

The dispersion relation can be written in this case in the following form

$$\begin{aligned} & \omega \left\{ (\rho_{11}\rho_{22} - \rho_{12}^2) \left(\frac{\omega}{k} \right)^2 - \mu^S \rho_{22} \right\} + \\ & + i\pi \left\{ (\rho_{11} + \rho_{22} + 2\rho_{12}) \left(\frac{\omega}{k} \right)^2 - \mu^S \right\} = 0, \end{aligned} \quad (371)$$

i.e.

$$\left(\frac{\omega}{k} \right)^2 = \frac{\omega r a + i \frac{\pi}{\rho_0^S}}{\omega r [a - r(1 - a)] + i \frac{\pi}{\rho_0^S} (1 + r)} c_S^2, \quad c_S^2 = \frac{\mu^S}{\rho_0^S}. \quad (372)$$

Consequently, neither the phase speed $\omega / \text{Re } k$ nor the attenuation $\text{Im } k$ of monochromatic shear waves is dependent on the coupling coefficient Q .

In the two limits of frequencies we have then the following solutions

$$\begin{aligned} \underline{\omega \rightarrow 0} : \quad & \lim_{\omega \rightarrow 0} \left(\frac{\omega}{\text{Re } k} \right)^2 = \frac{\mu^S}{\rho_0^S + \rho_0^F}, \quad \lim_{\omega \rightarrow 0} (\text{Im } k) = 0, \\ \underline{\omega \rightarrow \infty} : \quad & \lim_{\omega \rightarrow \infty} \left(\frac{\omega}{\text{Re } k} \right)^2 = \frac{\rho_{22}}{\rho_{11}\rho_{22} - \rho_{12}^2} \mu^S, \\ \lim_{\omega \rightarrow \infty} (\text{Im } k) = & \frac{\pi}{2\sqrt{\rho_0^S \mu^S}} \frac{1}{a^2} \sqrt{\frac{a}{a - r(1 - a)}}. \end{aligned} \quad (373)$$

The first result checks with the results of the classical one-component model commonly used in soil mechanics. The speed in the second one is identical with this of formula (359). Hence the propagation of the front of shear waves is identical with the propagation of monochromatic waves of infinite frequency. Let us notice that the attenuation in this limit is finite.

We demonstrate further properties of these monochromatic waves on a numerical example.

For longitudinal modes we obtain the dispersion relation

$$\begin{aligned} & [\rho_{11}\omega^2 - (\lambda^S + 2\mu^S)k^2 + i\pi\omega] [\rho_{22}\omega^2 - \kappa\rho_0^F k^2 + i\pi\omega] - \\ & - (\rho_{12}\omega^2 - Qk^2 - i\pi\omega)^2 = 0, \end{aligned} \quad (374)$$

or, after easy manipulations,

$$\begin{aligned} & \omega \left\{ [1 - r(1 - a)] \left(\frac{\omega}{k}\right)^2 - c_{P1}^2 \right\} \left\{ a \left(\frac{\omega}{k}\right)^2 - c_{P2}^2 \right\} + \\ & + \frac{1}{r} i \frac{\pi}{\rho_0^S} \left(\frac{\omega}{k}\right)^2 \left\{ (1 + r) \left(\frac{\omega}{k}\right)^2 - r c_{P2}^2 - c_{P1}^2 - 2 \frac{Q}{\rho_0^S} \right\} - \\ & - \frac{1}{r} \omega \left\{ r(1 - a) \left(\frac{\omega}{k}\right)^2 - \frac{Q}{\rho_0^S} \right\}^2 = 0. \end{aligned} \quad (375)$$

Let us check again two limits of frequencies: $\omega \rightarrow 0$, and $\omega \rightarrow \infty$.

In the first case we obtain

$$\begin{aligned} \underline{\omega \rightarrow 0} : \quad c_0 &:= \lim_{\omega \rightarrow 0} \left(\frac{\omega}{\text{Re } k} \right), \\ c_0^2 \left\{ (1 + r) c_0^2 - r c_{P2}^2 - c_{P1}^2 + 2 \frac{Q}{\rho_0^S} \right\} &= 0, \quad \lim_{\omega \rightarrow 0} (\text{Im } k) = 0. \end{aligned} \quad (376)$$

Obviously, we obtain two real solutions of this equation

$$\begin{aligned} \lim_{\omega \rightarrow 0} \left(\frac{\omega}{\text{Re } k} \right)^2 \Big|_1 &: = c_{oP1}^2 = \frac{c_{P1}^2 + r c_{P2}^2 + 2 \frac{Q}{\rho_0^S}}{1 + r} \equiv \frac{\lambda^S + 2\mu^S + \rho_0^F \kappa + 2 \frac{Q}{\rho_0^S}}{\rho_0^S + \rho_0^F}, \\ \lim_{\omega \rightarrow 0} \left(\frac{\omega}{\text{Re } k} \right)^2 \Big|_2 &: = c_{oP2}^2 = 0. \end{aligned} \quad (377)$$

These are squares of speeds of propagation of two longitudinal modes in the limit of zero frequency. Clearly, the second mode, P2-wave, does not propagate in this limit. Both limits are independent of tortuosity. The result (377) checks with the relation for the speed of longitudinal waves used in the classical one-component model of soil mechanics provided $Q = 0$.

In the second case we have

$$\underline{\omega \rightarrow \infty} : \quad c_\infty := \lim_{\omega \rightarrow \infty} \left(\frac{\omega}{\text{Re } k} \right),$$

$$r \left\{ [1 - r(1 - a)] c_\infty^2 - c_{P1}^2 \right\} \left\{ a c_\infty^2 - c_{P2}^2 \right\} - \left\{ r(1 - a) c_\infty^2 - \frac{Q}{\rho_0^S} \right\}^2 = 0. \quad (378)$$

This coincides with the relation (363). Consequently, the limit $\omega \rightarrow \infty$ gives indeed the properties of the front of acoustic longitudinal waves in the system.

Simultaneously we obtain the following attenuation in the limit of infinite frequencies

$$\lim_{\omega \rightarrow \infty} (\text{Im } k) = \frac{\pi \Gamma_1}{2 \rho_0^S r \Gamma_2}, \quad (379)$$

$$\begin{aligned} \Gamma_1 &= c_\infty \left[1 + r - \frac{1}{c_\infty^2} \left(c_{P1}^2 + r c_{P2}^2 + 2 \frac{Q}{\rho_0^S} \right) \right], \\ \Gamma_2 &= c_{P1}^2 \left(a - \frac{c_{P2}^2}{c_\infty^2} \right) + c_{P2}^2 \left(1 - r(1 - a) - \frac{c_{P1}^2}{c_\infty^2} \right) + 2 \frac{Q}{\rho_0^S} \left(1 - a - \frac{Q}{r \rho_0^S c_\infty^2} \right). \end{aligned}$$

Hence both limits of attenuation for the P1-wave and P2-wave are finite.

We proceed to the presentation of a numerical result in the whole range of frequencies $\omega \in [0, \infty)$. We use the following numerical data

$$\begin{aligned} c_{P1} &= 2500 \frac{\text{m}}{\text{s}}, & c_{P2} &= 1000 \frac{\text{m}}{\text{s}}, & c_S &= 1500 \frac{\text{m}}{\text{s}}, \\ \rho_0^S &= 2500 \frac{\text{kg}}{\text{m}^3}, & r &= 0.1, & \pi &= 10^8 \frac{\text{kg}}{\text{m}^3 \text{s}}, \\ Q &= 0.8 \text{ GPa}, & n_0 &= 0.4, & a &= 1.75. \end{aligned} \quad (380)$$

Speeds c_{P1}, c_{P2}, c_S , the mass density ρ_0^S (i.e. $\rho_0^{SR} = 4167 \frac{\text{kg}}{\text{m}^3}$ for the porosity $n_0 = 0.4$) and the fraction $r = \rho_0^F / \rho_0^S$ possess values typical for many granular materials under a confining pressure of a few atmospheres and saturated by water. In units standard for soil mechanics the permeability π corresponds to app. 0.1 Darcy. The coupling coefficient Q has been estimated by means of the Gassmann relation (see: Section 9). The tortuosity coefficient $a = 1.75$ follows from Berryman formula (352)₅.

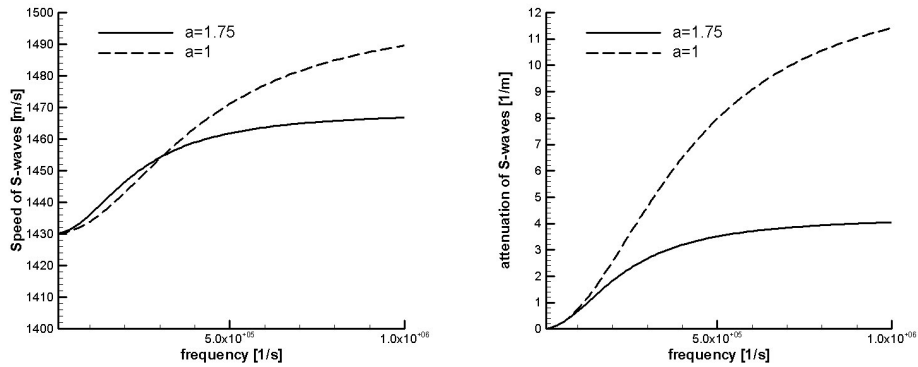


Figure 10: Speed of propagation and attenuation of monochromatic S-waves for two values of the tortuosity coefficient a : 1.75 (Biot), 1.00 (simple mixture).

Transversal waves described by the relation (372) are characterized by the following distribution of speeds and attenuation in function of frequency (Fig. 10). The solid lines

correspond to the solution of Biot's model and the dashed lines to the solution of the simple mixture model.

It is clear that the qualitative behavior of the speed of propagation is the same in both models. It is a few percent smaller in Biot's model than this in the simple mixture model in the range of high frequencies. A large quantitative difference between these models appears for the attenuation. In the range of higher frequencies it is much smaller in Biot's model, i.e. tortuosity decreases the dissipation of shear waves.

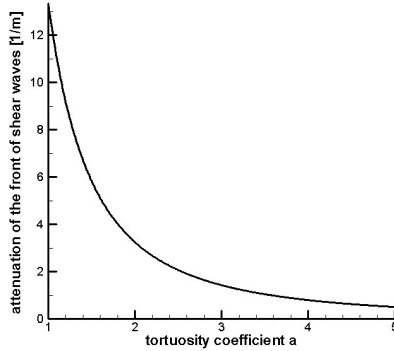


Figure 11: Attenuation of the front of shear waves in function of the tortuosity coefficient a .

The latter property is illustrated in Fig. 11 where we plot the attenuation of the front of shear waves, i.e. $\lim_{\omega \rightarrow \infty} \text{Im } k$, as a function of the tortuosity coefficient a . This behavior of attenuation indicates that damping of waves created by the tortuosity, which is connected in the macroscopic model to the relative velocity of components, is not related to scattering of waves on the microstructure. It is rather related to the decrease of the macroscopic diffusion velocity in comparison with the difference of velocities on the microscopic level due to the curvature of channels and volume averaging. Fluctuations are related solely to this averaging and not to temporal deviation from time averages (lack of ergodicity!).

The disastrous character of attenuation presented in Figure 11 indicates that an influence of tortuosity must be placed in the model somewhere else. This has been known already to Biot who speculated on the dependence of the diffusion coefficient on the frequency. This would be clearly an indication of some viscous effects or rather an influence of the microstructure on damping as the effect is present even in the case when the fluid in pores is inviscid. Such corrections are introduced until today rather *ad hoc* and have not been yet justified satisfactory by formal arguments of modeling.

We proceed to longitudinal waves. The solid lines on the following Figures correspond again to Biot's model, the dashed lines to the simple mixture model. In order to show separately the influence of tortuosity a and of the coupling Q we plot as well the solutions with $a = 1$ (dashed dotted lines) and the solutions with $Q = 0$ (dashed double dotted lines).

Even though similar again the quantitative differences are much more substantial for P1-waves (Fig. 12). This is primarily an influence of the coupling through partial stresses described by the parameter Q . The simple mixture model ($Q = 0, a = 1$) as well as Biot's

model with $Q = 0$ yield speeds of these waves different only a few percent (lower curves in the left diagram). The coupling Q shifts the curves to higher values and reduces the difference caused by the tortuosity. This result does not seem to be very realistic because the real differences between low frequency and high frequency speeds were measured in soils to be rather as big as indicated by the simple mixture model. This may be an indication that Gassmann relations give much too big values of the coupling parameter Q with respect to these indeed appearing in real granular materials.

Both the tortuosity a and the coupling Q reduce the attenuation quite considerably as indicated in the right Figure.

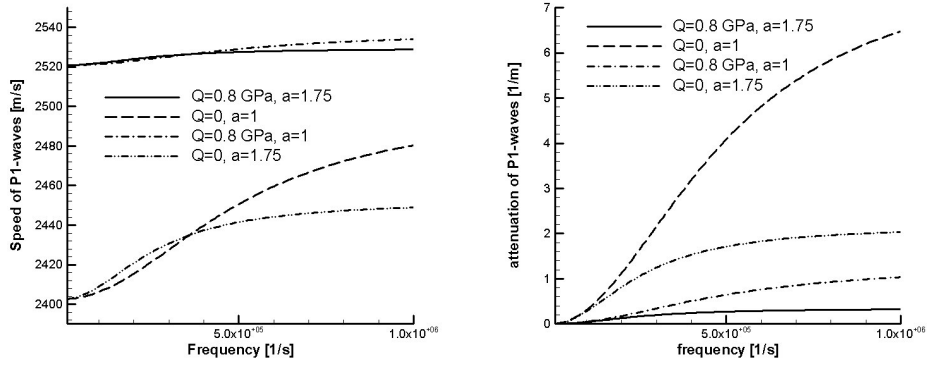


Figure 12: *Speed of propagation and attenuation of monochromatic P1-waves for various coupling parameters Q and tortuosity coefficients a .*

In spite of some claims in the literature the tortuosity a does not influence the existence of the slow (P2-) wave (Fig. 13). Speeds of this wave are again qualitatively similar in Biot's model and in the simple mixture model. The maximum differences appear in the range of high frequencies and reach some 35 percent. The same concerns the attenuation even though quantitative differences are not so big (app. 8 percent).

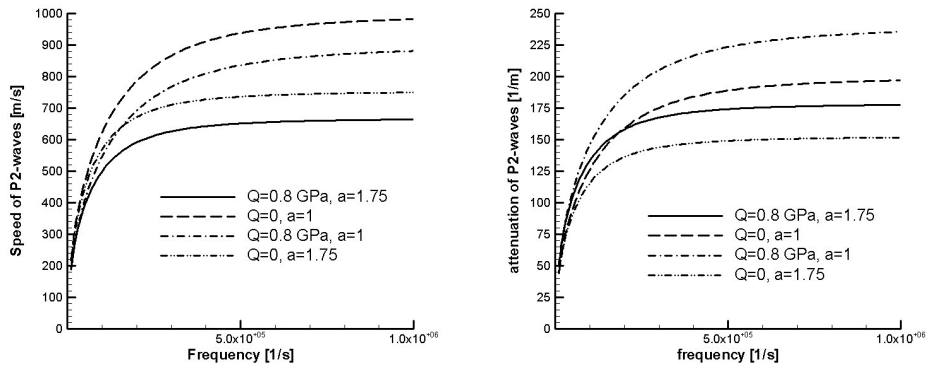


Figure 13: *Speed of propagation and attenuation of monochromatic P2-waves for various coupling parameters Q and tortuosity coefficients a .*

The above examples yield the following conclusions.

1° We have demonstrated on the example of acoustic waves that tortuosity a and the coupling parameter Q have a quantitative but not qualitative influence on results.

Comparison of results for Biot's model with these for the simple mixture model in which the tortuosity $a = 1$ and the coupling parameter $Q = 0$ shows that both models are hyperbolic provided the parameter Q satisfies a condition bounding this parameter from above. In particular, both models predict the existence of the P2-wave. Speeds and attenuations of monochromatic P1-, P2- and S-waves are qualitatively the same but there are quantitative discrepancies.

2° Tortuosity introduced to the model through the relative acceleration yields dissipation solely due to the modification of the relative motion. Namely if we assume the permeability coefficient $\pi = 0$ the dissipation in isothermal processes without relaxation of porosity vanishes. This is due to the fact that tortuosity, in contrast to porosity, is not introduced as a field described by its own field equation. This is an explanation of a rather unexpected behavior of attenuation of monochromatic waves. Inspection of figures shown in this Section makes clear that the presence of tortuosity $a \neq 1$ yields a smaller attenuation rather than bigger as it would be in the case of a dissipative field. This may be explained by the fact that tortuosity reduces the relative velocity $\mathbf{v}^F - \mathbf{v}^S$ and, consequently, it reduces the contribution to dissipation $\pi (\mathbf{v}^F - \mathbf{v}^S) \cdot (\mathbf{v}^F - \mathbf{v}^S)$.

3° We have demonstrated that a rather moderate value of the parameter Q suggested by the classical Gassmann relation for granular materials leads to an unreasonable increment of speeds of propagation and reduction of attenuation. In addition, the speed of propagation of monochromatic P1-waves becomes very flat as a function of frequency. This contradicts observations in soil mechanics and geotechnics and indicates that the Gassmann relation predicts too big values of this parameter.

10.4 Introduction to surface waves

The bulk waves presented above are the basis for the theory of surface waves. These waves are created due to the interaction of bulk waves with the boundary. The typical theoretical problem which yields such waves is the two-dimensional half-space problem of the classical elasticity. It is known (e.g. [47]) that in the case of the boundary between an elastic material and vacuum there exists a single surface wave – Rayleigh wave whose speed is a bit lower than the speed of transversal (shear) wave. In the case of an elastic layer on the elastic half-space, there may exist another surface wave – Love wave. On the other hand, if the elastic half-space is in contact with an ideal fluid, there exists a so-called Stoneley wave. A detailed review of this theory can be found in the book [31].

The fundamental problem of the theory of surface waves is the form of boundary conditions. As usual in theories of multicomponent systems with diffusion the problem of formulation of boundary conditions is connected with many additional physical problems stemming primarily from the fact that a relative motion of components leads to the creation of boundary layers. For isothermal processes in two-component models one expects two vectorial conditions on the boundary $\partial\mathcal{B}_0$. If the boundary is impermeable we have either purely kinematical conditions

$$\chi^S(\mathbf{X}, t) - \chi^S(\mathbf{X}, 0)|_{\mathbf{X} \in \partial\mathcal{B}_0} = 0, \quad \dot{\chi}^F(\mathbf{X}, t)|_{\mathbf{X} \in \partial\mathcal{B}_0} = 0, \quad (381)$$

or mixed conditions

$$(\mathbf{P}^S + \mathbf{P}^F) \mathbf{N}|_{\mathbf{X} \in \partial\mathcal{B}_0} = \mathbf{p}_{ext}, \quad \dot{\chi}^F(\mathbf{X}, t)|_{\mathbf{X} \in \partial\mathcal{B}_0} = 0. \quad (382)$$

The physical interpretation is obvious. In the first case we require that the boundary which is identified with the boundary of the skeleton does not move (the clamped condition), and that the velocity of the fluid component is identical with the velocity of the skeleton (lack of permeability). In the second case the second condition is identical, and the first one follows from the dynamic compatibility conditions. The right hand side of (382)₁ contains either an external, and given boundary loading \mathbf{p}_{ext} (in its Lagrangian form) or a total stress vector of the other body (continuity of stress vector following from dynamical compatibility conditions).

In the Eulerian description the conditions (382) have the form

$$(\mathbf{T}^S + \mathbf{T}^F) \mathbf{n}|_{\mathbf{x} \in \partial \mathcal{B}_t} = \mathbf{t}_{ext}, \quad \mathbf{v}^F - \mathbf{v}^S|_{\mathbf{x} \in \partial \mathcal{B}_t} = 0. \quad (383)$$

The situation is different in the case of permeable boundary. It was demonstrated by von Terzaghi in a Gedankenexperiment that the external loading cannot be distributed among components *a priori* on a permeable boundary, and we can solely require the condition of the form (382)₁ to hold. Consequently we need an additional vectorial condition in the case of two-component systems.

According to considerations connected with this Gedankenexperiment it is assumed that the flow of the fluid component through the permeable boundary is proportional to the real pressure difference on both sides of a boundary or interface between two different porous materials. According to the mass compatibility condition we have

$$\rho^F \dot{\mathbf{X}}^F \cdot \mathbf{N}|^- = \rho^F \dot{\mathbf{X}}^F \cdot \mathbf{N}|^+. \quad (384)$$

For this reason we do not use any signature for the boundary value of the mass flow. According to the above described assumption we have

$$\rho^F \dot{\mathbf{X}}^F \cdot \mathbf{N} = \alpha_0 \left[\left[\frac{\mathbf{P}^F}{n} \right] \right] \cdot \mathbf{F}^S. \quad (385)$$

In this relation the product $-\frac{1}{3}J^{S-1}\mathbf{P}^F \cdot \mathbf{F}^S \equiv -\frac{1}{3}J^{S-1} \text{tr } \mathbf{P}^F \mathbf{F}^{ST}$ is identical with the partial pressure in Eulerian description. The coefficient α_0 denotes the *surface permeability coefficient* related to the Lagrangian image of the boundary or interface. Its existence is connected with the fact that the flow of the fluid component from the negative side of the surface to its positive side must overcome obstacles connected with the change of geometrical properties of the neighboring media. In our model this is reflected primarily by different porosities on both sides of the surface. It is reasonable to assume that such a change of flow conditions yields the existence of a boundary layer which is replaced by a jump condition (385) with a phenomenological coefficient α_0 .

It is easier to appreciate the structure of condition (385) in the Eulerian description

$$\rho_t^F (\mathbf{v}^F - \mathbf{v}^S) \cdot \mathbf{n} = \alpha \left(p^{F-} - \frac{n^-}{n^+} p^{F+} \right), \quad \alpha := \frac{3\alpha_0}{n^-} (\mathbf{N} \cdot \mathbf{C}^{S-1} \mathbf{N})^{-\frac{1}{2}}, \quad (386)$$

where \mathbf{n} is the unit normal vector of the surface in its current configuration.

If the surface is an external boundary we have $n^+ = 1$, and p^{F+} is an external pressure which must be given on the surface in addition to the external loading appearing in (383).

The above condition for permeable boundary has been introduced by Deresiewicz in 1962 [17] in the analysis of surface waves.

Let us mention in passing that this art of boundary conditions can be introduced in multicomponent models based on partial momentum equations in contrast to scalar models following from the application of Darcy's law in mass balance equations alone. Models of the latter type leading to nonlinear parabolic reaction-diffusion equations dominate in the mathematical literature on porous materials, they are frequently considered to be the theories of porous materials *per se*, and usually require rather artificial boundary conditions like a continuity of the pore pressure.

The boundary condition (386) has been tested in classical problems of consolidation as well as in processes of coupling between diffusion and adsorption. It has been found out that it checks very well with expectations. Another class of problems in which this condition plays an important role are surface waves.

Certainly the condition (386) determines only one component of the vector (in the direction of the normal \mathbf{n}) which we have to prescribe on the boundary. We have to add a condition on the tangential component of the relative velocity. In the case of viscous fluids the problem is similar to that which we discussed above and we have to account for the boundary layer. We consider in these notes solely ideal fluids and in this case we deal with a sticking condition

$$(\mathbf{v}^{F\pm} - \mathbf{v}^{F\pm} \cdot \mathbf{nn}) - (\mathbf{v}^S - \mathbf{v}^S \cdot \mathbf{nn}) = 0, \quad (387)$$

for the interface. It reduces to the single condition on the external boundary.

Conditions (386), (387) together with the conditions (383)₁ and (384) form the full set of boundary conditions for the two-component porous material filled with an ideal fluid.

Let us mention that the additional porosity balance equation does not require boundary conditions and it yields effects similar to these of usual evolution equations for internal (microstructural) variables.

10.5 Surface waves for the contacts: porous body/vacuum, porous body/liquid; asymptotic properties of the dispersion relation

10.5.1 Preliminaries

We have seen in Subsection 10.3 that the two-component model of porous materials considered in these notes yields three modes of propagation of bulk waves. It means that we must expect instead of a single Rayleigh surface wave of a classical single component elastic continuum a higher number of surface modes of propagation. We show that this is the case.

Let us first briefly recall the construction of classical Rayleigh waves in linear elasticity. These follow from the superposition of longitudinal and transversal waves which are solutions of two wave equations

$$\begin{aligned} \frac{\partial^2 \mathbf{u}_L}{\partial t^2} &= c_L^2 \Delta \mathbf{u}_L, & c_L^2 &:= \frac{\lambda + 2\mu}{\rho}, & \text{rot } \mathbf{u}_L &= 0, \\ \frac{\partial^2 \mathbf{u}_T}{\partial t^2} &= c_T^2 \Delta \mathbf{u}_T, & c_T^2 &:= \frac{\mu}{\rho}, & \text{div } \mathbf{u}_T &= 0, \end{aligned} \quad (388)$$

where λ, μ are Lamé elasticity constants, ρ denotes the mass density, and the displacement $\mathbf{u} = \mathbf{u}_L + \mathbf{u}_T$. If we consider now the boundary value problem for the half-space $y > 0$ with the free boundary $y = 0$ then we can easily show that there exist solutions of the following general form

$$\begin{aligned} \mathbf{u} = & (u^L \exp(-\gamma^L y) + u^T \exp(-\gamma^T y)) \sin(k(x - U_R t)) \mathbf{e}_x + \\ & + \left(u^L \frac{\gamma^L}{k} \exp(-\gamma^L y) + u^T \frac{k}{\gamma^T} \exp(-\gamma^T y) \right) \cos(k(x - U_R t)) \mathbf{e}_y, \quad U_R < U_T, \end{aligned} \quad (389)$$

where $\mathbf{e}_x, \mathbf{e}_y$ are unit base vectors in directions of x and y axes, respectively, u^L, u^T are real amplitudes and γ^L, γ^T, k with $\frac{\gamma^L}{k} = O(1), \frac{\gamma^T}{k} = O(1)$ are real constants following from the dispersion relations

$$\begin{aligned} \left(\frac{\gamma^L}{k} \right)^2 &= 1 - \frac{c_R^2}{c_L^2}, \quad \left(\frac{\gamma^T}{k} \right)^2 = 1 - \frac{c_R^2}{c_T^2}, \\ \left(2 - \frac{c_R^2}{c_T^2} \right)^2 &= 4 \sqrt{\left(1 - \frac{c_R^2}{c_L^2} \right)} \sqrt{\left(1 - \frac{c_R^2}{c_T^2} \right)}, \end{aligned} \quad (390)$$

which are, in turn, a result of solvability of equations (388) and of the homogeneity of boundary conditions, respectively. It is clearly seen that the wave described by (389) propagates with speed c_R , and it attenuates very fast with the depth y . This is the reason for calling it a *surface wave*. Obviously the displacement $\mathbf{u} = u_x \mathbf{e}_x + u_y \mathbf{e}_y$ describes ellipses

$$\frac{u_x^2}{(u^L e^{-\gamma^L y} + u^T e^{-\gamma^T y})^2} + \frac{u_y^2}{\left(u^L \frac{\gamma^L}{k} e^{-\gamma^L y} + u^T \frac{k}{\gamma^T} e^{-\gamma^T y} \right)^2} = 1. \quad (391)$$

These are local trajectories of materials particles.

It is important that surface waves do not attenuate along the boundary. A simple geometrical argument shows then that their dispersion in the case of the point source is much slower than this of bulk waves. Namely bulk waves are spherical and, consequently, their amplitudes decay as $\frac{1}{r^3}$, r being the distance from the source while surface waves are cylindrical, and for this reason their amplitudes decay as $\frac{1}{r^2}$. This makes surface waves very attractive in practical applications.

10.5.2 Governing equations

We proceed to describe surface waves in poroelastic materials saturated with a fluid. The detailed analysis both theoretical as well as numerical can be found in contributions of B. Albers and K. Wilmanski to the book [31]. We present here only a brief summary of this complex problem.

As mentioned above the theory of surface waves in two-component systems differs qualitatively from such a theory for one-component continua. Such waves are produced in linear models by a combination of bulk waves. In the case of a one-component continuum there are two bulk modes of propagation which yield a single Rayleigh wave. For two-component systems we have three bulk modes: P1-waves, P2-waves and S-waves which produce two surface modes in the case of impermeable boundary. For the permeable

boundary, i.e. for the case of an additional system – a fluid in the exterior, there may exist three surface modes, etc. In addition, as all these waves are dissipative and there may exist additional so-called leaky modes.

In this Subsection we consider surface waves in two-component homogeneous poroelastic materials with an impermeable boundary. However, we indicate as well some properties related to the permeable boundary condition. This condition has been proposed in 1962 by Deresiewicz [17]. The analysis is based on the simple mixture model. We limit the attention solely to high and low frequency ranges. A much more extensive article of B. Albers in the book [31] contains also a numerical analysis of the problem in the full frequency range. We leave entirely open the problem of existence which is at least as complicated as in the case of single component materials.

To the end of this Section we quote a few results obtained within Biot's model. As this model is much more complicated than the simple mixture model results are limited only to some special cases.

10.5.3 Compatibility conditions and dispersion relation

As discussed in [67] we seek a solution of the set of field equations which we obtain from Biot's equations by the substitution $Q = 0, a = 1$. It is convenient to introduce the displacement vector \mathbf{u}^S for the skeleton, and, formally, the displacement vector \mathbf{u}^F for the fluid. The latter is introduced solely for the technical symmetry of considerations and it does not have any physical bearing. Then

$$\begin{aligned}\mathbf{u}^S &= \text{grad } \varphi^S + \text{rot } \boldsymbol{\psi}^S, & \mathbf{v}^S &= \frac{\partial \mathbf{u}^S}{\partial t}, & \mathbf{e}^S &= \text{sym grad } \mathbf{u}^S, \\ \mathbf{u}^F &= \text{grad } \varphi^F + \text{rot } \boldsymbol{\psi}^F, & \mathbf{v}^F &= \frac{\partial \mathbf{u}^F}{\partial t},\end{aligned}\quad (392)$$

where $\varphi^S, \boldsymbol{\psi}^S, \varphi^F, \boldsymbol{\psi}^F$ are two pairs of potentials analogous to those which we were using in the classical elasticity model.

We choose the axes with the downward orientation of the z -axis and the x -axis in the direction of propagation of the wave. As the problem is assumed to be two-dimensional we make the following ansatz for solutions

$$\begin{aligned}\varphi^S &= A^S(z) \exp[i(kx - \omega t)], & \varphi^F &= A^F(z) \exp[i(kx - \omega t)], \\ \psi_y^S &= B^S(z) \exp[i(kx - \omega t)], & \psi_y^F &= B^F(z) \exp[i(kx - \omega t)], \\ \psi_x^S &= \psi_z^S = \psi_x^F = \psi_z^F = 0,\end{aligned}\quad (393)$$

and

$$\begin{aligned}\rho^S - \rho_0^S &= A_\rho^S(z) \exp[i(kx - \omega t)], & \rho^F - \rho_0^F &= A_\rho^F(z) \exp[i(kx - \omega t)], \\ n - n_0 &= A^\Delta \exp[i(kx - \omega t)].\end{aligned}\quad (394)$$

Substitution in field equations leads after straightforward calculations to the following compatibility conditions for $z \geq 0$

$$\begin{aligned}B^F &= \frac{i\pi}{\rho_0^F \omega + i\pi} B^S, & A^\Delta &= -\frac{n_0 \omega \tau}{i + \omega \tau} \left(\frac{d^2}{dz^2} - k^2 \right) (A^F - A^S), \\ A_\rho^S &= -\rho_0^S \left(\frac{d^2}{dz^2} - k^2 \right) A^S, & A_\rho^F &= -\rho_0^F \left(\frac{d^2}{dz^2} - k^2 \right) A^F,\end{aligned}\quad (395)$$

as well as

$$\left[\kappa \left(\frac{d^2}{dz^2} - k^2 \right) + \omega^2 \right] A^F + \left[\frac{n_0 \beta \omega \tau}{\rho_0^F (i + \omega \tau)} \left(\frac{d^2}{dz^2} - k^2 \right) + \frac{i\pi}{\rho_0^F} \omega \right] (A^F - A^S) = 0, \quad (396)$$

$$\left[\frac{\lambda^S + 2\mu^S}{\rho_0^S} \left(\frac{d^2}{dz^2} - k^2 \right) + \omega^2 \right] A^S - \left[\frac{n_0 \beta \omega \tau}{\rho_0^S (i + \omega \tau)} \left(\frac{d^2}{dz^2} - k^2 \right) + \frac{i\pi}{\rho_0^S} \omega \right] (A^F - A^S) = 0, \quad (397)$$

$$\left[\frac{\mu^S}{\rho_0^S} \left(\frac{d^2}{dz^2} - k^2 \right) + \omega^2 \right] B^S + \frac{i\pi \rho_0^F}{\rho_0^S (\rho_0^F \omega + i\pi)} \omega^2 B^S = 0. \quad (398)$$

It is convenient to introduce a dimensionless notation. In order to do so we define the following auxiliary quantities

$$\begin{aligned} c_s &= \frac{c_S}{c_{P1}} < 1, & c_f &= \frac{c_{P2}}{c_{P1}}, & \pi' &= \frac{\pi \tau}{\rho_0^S} > 0, & \beta' &= \frac{n_0 \beta}{\rho_0^S c_{P1}^2} > 0, \\ r &= \frac{\rho_0^F}{\rho_0^S} < 1, & z' &= \frac{z}{c_{P1} \tau}, & k' &= k c_{P1} \tau, & \omega' &= \omega \tau. \end{aligned} \quad (399)$$

where the velocities c_{P1}, c_{P2}, c_S are defined by (361), (364) and, in the simple mixture model, they describe the velocities of fronts of bulk S-wave and P1-, P2-waves, respectively. These are, of course, identical with the limits of bulk phase velocities for $\omega \rightarrow \infty$. As we neglect processes of relaxation of porosity, the reference time τ can be chosen arbitrarily.

As we have already mentioned, we neglect further the influence of the nonequilibrium changes of porosity, i.e. $\beta = 0$. In the compatibility relations derived in this Subsection we still keep it in the relations in order to show the way in which this influence enters the model if not ignored.

Further we omit the prime for typographical reasons. Substitution of (399) in equations (396), (398) yields

$$\begin{aligned} \left[c_f^2 \left(\frac{d^2}{dz^2} - k^2 \right) + \omega^2 \right] A^F + \left[\frac{\beta \omega}{r (i + \omega)} \left(\frac{d^2}{dz^2} - k^2 \right) + i \frac{\pi}{r} \omega \right] (A^F - A^S) &= 0, \\ \left[\left(\frac{d^2}{dz^2} - k^2 \right) + \omega^2 \right] A^S - \left[\frac{\beta \omega}{i + \omega} \left(\frac{d^2}{dz^2} - k^2 \right) + i \pi \omega \right] (A^F - A^S) &= 0, \\ \left[c_s^2 \left(\frac{d^2}{dz^2} - k^2 \right) + \omega^2 + \frac{i \pi \omega}{\omega + i \frac{\pi}{r}} \right] B^S &= 0. \end{aligned} \quad (400)$$

This differential eigenvalue problem can be easily solved because the matrix of coefficients for homogeneous materials is independent of z . This is different from the case of waves in heterogeneous materials (see: [31]). Consequently, we seek solutions in the form

$$A^F = A_f^1 e^{\gamma_1 z} + A_f^2 e^{\gamma_2 z}, \quad A^S = A_s^1 e^{\gamma_1 z} + A_s^2 e^{\gamma_2 z}, \quad B^S = B_s e^{\zeta z}, \quad (401)$$

where, due to the chosen direction of the z -axis, the exponents $\gamma_1, \gamma_2, \zeta$ must possess negative real parts. This is the existence requirement for surface waves. Substitution in (400) yields them in the form

$$\left(\frac{\zeta}{k} \right)^2 = 1 - \frac{1}{c_s^2} \left(1 + \frac{i \pi}{\omega + i \frac{\pi}{r}} \right) \left(\frac{\omega}{k} \right)^2, \quad (402)$$

and

$$\begin{aligned} & \left[c_f^2 + \left(c_f^2 + \frac{1}{r} \right) \frac{\beta\omega}{i+\omega} \right] \left[\left(\frac{\gamma}{k} \right)^2 - 1 \right]^2 + \left[1 + \left(1 + \frac{1}{r} \right) \frac{i\pi}{\omega} \right] \left(\frac{\omega}{k} \right)^4 \\ & + \left[1 + c_f^2 + \left(1 + \frac{1}{r} \right) \frac{\beta\omega}{i+\omega} + \left(c_f^2 + \frac{1}{r} \right) \frac{i\pi}{\omega} \right] \left[\left(\frac{\gamma}{k} \right)^2 - 1 \right] \left(\frac{\omega}{k} \right)^2 = 0. \end{aligned} \quad (403)$$

Simultaneously we obtain the following relations for eigenvectors

$$\mathbf{R}^1 = (B_s, A_s^1, A_f^1)^T, \quad \mathbf{R}^2 = (B_s, A_s^2, A_f^2)^T, \quad (404)$$

where

$$A_f^1 = \delta_f A_s^1, \quad A_s^2 = \delta_s A_f^2, \quad (405)$$

$$\delta_f := \frac{1}{r} \frac{\frac{\beta\omega}{i+\omega} \left[\left(\frac{\gamma_1}{k} \right)^2 - 1 \right] + \frac{i\pi}{\omega} \frac{\omega^2}{k^2}}{\left(c_f^2 + \frac{1}{r} \frac{\beta\omega}{i+\omega} \right) \left[\left(\frac{\gamma_1}{k} \right)^2 - 1 \right] + \left(\frac{\omega}{k} \right)^2 + \frac{i\pi}{\omega r} \frac{\omega^2}{k^2}}, \quad (406)$$

$$\delta_s := \frac{\frac{\beta\omega}{i+\omega} \left[\left(\frac{\gamma_2}{k} \right)^2 - 1 \right] + \frac{i\pi}{\omega} \frac{\omega^2}{k^2}}{\left(1 + \frac{\beta\omega}{i+\omega} \right) \left[\left(\frac{\gamma_2}{k} \right)^2 - 1 \right] + \left(\frac{\omega}{k} \right)^2 + \frac{i\pi}{\omega} \frac{\omega^2}{k^2}}. \quad (407)$$

The above solution for the exponents still leaves three unknown constants B_s, A_f^2, A_s^1 which must be specified from boundary conditions. This is the subject of the next Subsection.

For technical reasons, we limit the attention solely to the limit problems in the range of high and low frequencies.

In the case of **high frequency approximation** we immediately obtain from relations (402) and (403)

$$\begin{aligned} \frac{1}{\omega} \ll 1 : \quad & \left(\frac{\zeta}{k} \right)^2 = 1 - \frac{1}{c_s^2} \left(\frac{\omega}{k} \right)^2, \\ & \left(\frac{\gamma_1}{k} \right)^2 = 1 - \left(\frac{\omega}{k} \right)^2, \quad \left(\frac{\gamma_2}{k} \right)^2 = 1 - \frac{1}{c_f^2} \left(\frac{\omega}{k} \right)^2, \end{aligned} \quad (408)$$

and

$$\delta_f = \delta_s = 0 \quad \Rightarrow \quad \mathbf{R}^1 = (B_s, A_s^1, 0)^T, \quad \mathbf{R}^2 = (B_s, 0, A_f^2)^T. \quad (409)$$

For the case of **low frequency approximation** the equation (403) becomes singular. It can be written in the following form

$$\begin{aligned} \omega \ll 1 : \quad & c_f^2 \omega^2 \left[\left(\frac{\gamma}{k} \right)^2 - 1 \right]^2 + \omega \left[\omega + i\pi \left(1 + \frac{1}{r} \right) \right] \left(\frac{\omega}{k} \right)^4 + \\ & + \left[\omega \left(1 + c_f^2 \right) + i\pi \left(c_f^2 + \frac{1}{r} \right) \right] \omega \left[\left(\frac{\gamma}{k} \right)^2 - 1 \right] \left(\frac{\omega}{k} \right)^2 = 0. \end{aligned} \quad (410)$$

Making the following substitution

$$W := \omega \left[\left(\frac{\gamma}{k} \right)^2 - 1 \right] + \omega \left(\frac{\omega}{k} \right)^2 \frac{1 + c_f^2}{2c_f^2}, \quad (411)$$

we obtain a quadratic equation for W

$$\begin{aligned} c_f^2 W^2 + i\pi \left(c_f^2 + \frac{1}{r} \right) \left(\frac{\omega}{k} \right)^2 W - \\ - \left\{ i\pi \left[\frac{(c_f^2 + \frac{1}{r})(1 + c_f^2)}{2c_f^2} - \left(1 + \frac{1}{r} \right) \right] \left(\frac{\omega}{k} \right)^4 \right\} \omega + O(\omega^2) = 0, \end{aligned} \quad (412)$$

which for small ω can be solved by the regular perturbation method

$$W = W_0 + \omega W_1 + O(\omega^2). \quad (413)$$

After easy calculations we obtain

$$W = \begin{cases} \left[\frac{1+c_f^2}{2c_f^2} - \frac{r+1}{rc_f^2+1} \right] \left(\frac{\omega}{k} \right)^2 \omega, \\ - \left[\frac{1+c_f^2}{2c_f^2} - \frac{r+1}{rc_f^2+1} \right] \left(\frac{\omega}{k} \right)^2 \omega - i\pi \frac{rc_f^2+1}{rc_f^2} \left(\frac{\omega}{k} \right)^2 \end{cases}. \quad (414)$$

Bearing the relation (411) in mind we arrive at the following results for the exponents

$$\begin{aligned} \omega \ll 1 : \quad \left(\frac{\zeta}{k} \right)^2 &= 1 - \frac{r+1}{c_s^2} \left(\frac{\omega}{k} \right)^2, \\ \left(\frac{\gamma_1}{k} \right)^2 &= 1 - \frac{r+1}{rc_f^2+1} \left(\frac{\omega}{k} \right)^2, \end{aligned} \quad (415)$$

$$\left(\frac{\gamma_2}{k} \right)^2 = 1 - \frac{rc_f^4+1}{c_f^2(rc_f^2+1)} \left(\frac{\omega}{k} \right)^2 - \frac{i\pi}{\omega} \frac{rc_f^2+1}{rc_f^2} \left(\frac{\omega}{k} \right)^2,$$

and for the coefficients of amplitudes

$$\delta_f = 1 - \frac{\omega r}{i\pi} \frac{1 - c_f^2}{1 + rc_f^2}, \quad \delta_s = -rc_f^2 \left(1 - \frac{\omega r}{i\pi} \frac{1 - c_f^2}{1 + rc_f^2} \right). \quad (416)$$

Obviously due to the singular character of the equation (410) the last contribution to $\frac{\gamma_2}{k}$ becomes singular for $\omega \rightarrow 0$.

10.5.4 Boundary value problems for surface waves

In order to determine surface waves in saturated poroelastic medium we need conditions for $z = 0$. We discuss in some details the problem in which this boundary is **impermeable**, and a poroelastic medium is in contact with **vacuum**. According to Subsection 10.4 boundary conditions have then the form

$$T_{13}|_{z=0} \equiv T_{13}^S|_{z=0} = \mu^S \left(\frac{\partial u_1^S}{\partial z} + \frac{\partial u_3^S}{\partial x} \right) \Big|_{z=0} = 0, \quad (417)$$

$$\begin{aligned} T_{33}|_{z=0} &\equiv (T_{33}^S - p^F)|_{z=0} = \\ &= c_{P1}^2 \rho_0^S \left(\frac{\partial u_1^S}{\partial x} + \frac{\partial u_3^S}{\partial z} \right) - 2c_S^2 \rho_0^S \frac{\partial u_1^S}{\partial x} - c_{P2}^2 (\rho^F - \rho_0^F) \Big|_{z=0} = 0, \end{aligned} \quad (418)$$

$$\frac{\partial}{\partial t} (u_3^F - u_3^S) \Big|_{z=0} = 0, \quad (419)$$

where $T_{13}, T_{13}^S, T_{33}, T_{33}^S$ are components of stress tensors and the first two conditions mean that the surface $z = 0$ is stress-free (far-field approximation), and the last condition means that there is no transport of fluid mass through this surface (impermeable boundary). u_1^S, u_3^S denote the components of the displacement \mathbf{u}^S in the direction of x -axis and z -axis, respectively, while u_3^F is the z -component of the displacement \mathbf{u}^F .

In the case of a permeable boundary neither the condition (417) nor the condition (419) would hold.

The first condition would have to possess the right-hand side reflecting the external pressure p_{ext} appearing in the fluid outside of the porous material. This change would appear as well in the case of impermeable boundary when we did not have the vacuum outside.

Condition (419) which reflects the fact that the impermeable boundary is **material** for both the solid and fluid component would have to describe mass transport through the surface specified by a relation to a driving force. According to the proposition of Deresiewicz and Skalak [17] such a driving force is proportional to the difference of pore pressures on both sides of the boundary

$$\rho_0^F \frac{\partial}{\partial t} (u_3^F - u_3^S) - \alpha (p^F - n_0 p_{ext}) \Big|_{z=0} = 0, \quad (420)$$

where α denotes a surface permeability coefficient and p_{ext} is an external pressure.

The coefficient α is an overall macroscopic description of a boundary layer which is created by the flow of the fluid component from conditions specified by the porous material (i.e. by the permeability π , porosity n , a geometry of the microscopic vicinity of the boundary such as a shape of openings of channels, their average orientation with respect to the surface normal, etc.) to the free space of a pure fluid. It is clear that the limit $\alpha \rightarrow 0$ corresponds to the impermeable (sealed) boundary, and the limit $\alpha \rightarrow \infty$ corresponds to the continuity of pressure in the fluid: $p^F = n_0 p_{ext}$. Such a boundary condition is used, for instance, in theories of porous materials with a rigid skeleton which are used in the description of various geotechnical diffusion and seepage processes.

In addition, for the permeable boundary we have to account for the continuity of the mass flux through the boundary. This additional boundary condition is necessary with respect to the existence of an additional constant in the solution for the exterior (in the range $z < 0$).

Substitution of results of the previous Subsection in boundary conditions (417)-(419) yields the following equations for three unknown constants B_s, A_f^2, A_s^1

$$\mathbf{A}\mathbf{X} = \mathbf{0}, \quad (421)$$

where

$$\mathbf{A} := \begin{pmatrix} \left(\frac{\zeta}{k}\right)^2 + 1 & 2i\frac{\gamma_2}{k}\delta_s & 2i\frac{\gamma_1}{k} \\ -2ic_s^2\frac{\zeta}{k} & \left[\left(\frac{\gamma_2}{k}\right)^2 - 1 + 2c_s^2\right]\delta_s + & \left(\frac{\gamma_1}{k}\right)^2 - 1 + 2c_s^2 + \\ & + rc_f^2\left[\left(\frac{\gamma_2}{k}\right)^2 - 1\right] & + rc_f^2\left[\left(\frac{\gamma_1}{k}\right)^2 - 1\right]\delta_f \\ i\frac{r\omega}{r\omega + i\pi} & -(\delta_s - 1)\frac{\gamma_2}{k} & (\delta_f - 1)\frac{\gamma_1}{k} \end{pmatrix}, \quad (422)$$

$$\mathbf{X} := \left(B_s, A_f^2, A_s^1 \right)^T.$$

This homogeneous set yields the **dispersion relation**: $\det \mathbf{A} = 0$ determining the $\omega - k$ relation. We investigate separately solutions of this equation for high and low frequencies.

10.5.5 High frequency approximation

In the case of high frequencies $\frac{1}{\omega} \ll 1$ we have $\delta_s = \delta_f = 0$ and the dispersion relation follows in the form

$$\mathcal{P}_R \sqrt{1 - \frac{1}{c_f^2} \left(\frac{\omega}{k}\right)^2} + \frac{r}{c_s^4} \left(\frac{\omega}{k}\right)^4 \sqrt{1 - \left(\frac{\omega}{k}\right)^2} = 0, \quad (423)$$

where

$$\mathcal{P}_R := \left(2 - \frac{1}{c_s^2} \left(\frac{\omega}{k}\right)^2\right)^2 - 4\sqrt{1 - \left(\frac{\omega}{k}\right)^2} \sqrt{1 - \frac{1}{c_s^2} \left(\frac{\omega}{k}\right)^2}. \quad (424)$$

Hence for $r = 0$ the relation (423) reduces to $\mathcal{P}_R = 0$ which is the Rayleigh dispersion relation for single component continua. Otherwise we obtain the relation identical with this analyzed by I. Edelman and K. Wilmanski [19] in the limit of short waves (i.e. $\frac{1}{k} \ll 1$). Consequently, the conclusions for this case are the same as well. As shown in the paper [19] the equation (423) possesses two roots defining two surface waves: a true Stoneley wave which propagates with the finite attenuation and with the velocity a bit smaller than c_f as well as a generalized Rayleigh wave which is leaky (i.e. it radiates the energy to the P2-wave) and propagates with the velocity c_R : $c_f < c_R < c_s$. The Rayleigh wave is leaky because its attenuation is unbounded, i.e. such a wave cannot exist in the range of high frequencies. Immediately after the initiation, it transforms into bulk waves.

These results are not very surprising because the dispersion relation (423) is identical with the dispersion relation in for the so-called Stoneley-Scholte wave [47]. The only difference is that the real Stoneley-Scholte wave propagates on both sides of the interface and the above presented wave propagates solely below the boundary ($z > 0$) in the porous medium.

The detailed description of these waves can be found in the article of B. Albers in [31].

10.5.6 Low frequency approximation

If we account for the relations (415) and (416) in the condition $\det \mathbf{A} = 0$ then we obtain the dispersion relation reflecting a dependence of $\frac{\omega}{k}$ on ω . The expansion with respect to $\sqrt{\omega}$ yields the identity in the zeroth order and the following relation for the higher order

$$\left(\frac{\omega}{k}\right) \left\{ \left(2 - \frac{r+1}{c_s^2} \left(\frac{\omega}{k}\right)^2\right)^2 - 4\sqrt{1 - \frac{r+1}{c_s^2} \left(\frac{\omega}{k}\right)^2} \sqrt{1 - \frac{r+1}{rc_f^2 + 1} \left(\frac{\omega}{k}\right)^2} \right\} + O(\sqrt{\omega}) = 0. \quad (425)$$

Clearly we obtain two solutions:

1. Rayleigh wave whose velocity is different from zero in the limit $\omega \rightarrow 0$ and whose attenuation is of the order $O(\sqrt{\omega})$. The relation for the velocity reminds the relation (424) with the velocities of bulk waves replaced by the low frequency limits. Namely we have

$$\frac{r+1}{c_s^2} = c_{P1}^2 \frac{\rho_0^S + \rho_0^F}{\mu^S} \equiv \frac{c_{P1}^2}{c_{oS}^2}, \quad \frac{r+1}{rc_f^2 + 1} = c_{P1}^2 \frac{\rho_0^S + \rho_0^F}{\lambda^S + 2\mu^S + \rho_0^F \kappa} \equiv \frac{c_{P1}^2}{c_{oP1}^2}. \quad (426)$$

Consequently

$$\left(2 - \frac{c_{P1}^2}{c_{oS}^2} \left(\frac{\omega}{k}\right)^2\right)^2 - 4\sqrt{1 - \frac{c_{P1}^2}{c_{oS}^2} \left(\frac{\omega}{k}\right)^2} \sqrt{1 - \frac{c_{P1}^2}{c_{oP1}^2} \left(\frac{\omega}{k}\right)^2} = 0. \quad (427)$$

2. The Stoneley wave has the velocity of propagation of the order $O(\sqrt{\omega})$. Hence, it goes to zero in the same way as the velocity of propagation of the P2-wave.

10.5.7 Remarks on modelling surface waves by Biot's model and the simple mixture model

The results for a two-component model of porous solid-fluid mixtures presented in this Section should be compared with those obtained by means of the Biot's model and with experimental observations. We shall not go into details of such a comparison in this work. However, as mentioned before, there is a very good qualitative agreement of both models as far as propagation of acoustic waves is concerned. Velocities of bulk waves are influenced by the coupling parameter Q but this influence reflected in high frequency – low frequency relations seems to be too strong for values of this parameter following

from the classical Gassmann relations. The influence of tortuosity a on the velocities of propagation is rather small and, simultaneously, essential changes of attenuation do not correspond to the physical inside, particularly to mechanisms of scattering of waves, of the morphology of porous materials in spite of some claims in the literature.

Neither bulk waves nor surface waves reveal any qualitative differences between Biot's model and the simple mixture model. It can be expected that ranges of existence of different surface modes are different for both models but results of analysis of this problem are not yet available.

It should be mentioned that results for surface waves within the Biot's model are often limited to high frequency limit. Some early results of Deresiewicz for low frequencies do not depart from those obtained within the simple mixture model.

Certainly, it should be born in mind that the simple mixture model must be quantitatively a worse approximation than Biot's model because it does not contain natural physical couplings. However, it is known from the theory of mixture of fluids that many results of the simple mixture theory are good enough for some practical purposes. This seems to be also the case for porous materials as far as a qualitative analysis of acoustic waves is concerned.

11 Mass exchange in porous materials

11.1 Adsorption for large channel diameter

Mass exchange between components of porous, and granular materials belongs to the most important problems of practical bearing within theories of such materials. This is connected primarily with a very large internal surface per unit volume on which the exchange takes place. For instance in sandstones it reaches the value of $1.5 \times 10^5 \frac{m^2}{m^3}$ in comparison with $6 \frac{m^2}{m^3}$ for the external surface. This property is used in many technological processes. For instance in the growth of SiC crystals by sublimation the vapor of silicium flows through a porous graphite wall in which it forms various carbide connections. A charcoal granular material is also used in gas masks. Lungs, many filters and chemical reactors are made of porous materials for the same reason. Transport of pollutants by ground water in soils is an important example of such processes appearing spontaneously in nature.

Classically processes of mass exchange in porous materials were divided into two classes of *chemical and physical adsorption*. This classification seems to be not very sharp but it is still useful by construction of various macroscopic models. In the case of chemical adsorption we deal with exchange of mass between skeleton and one or more fluid components in which particles build chemical bindings. In contrast to such processes in a physical adsorption particles of skeleton and of a fluid component form weak van der Waals bindings. The first type of exchange is connected with essential thermal effects connected with a release or absorption of energy, i.e. with the latent heat of reaction. On the other hand the heat of reaction by physical adsorption is very small and we use the approximation of isothermal processes. We discuss such a model in this Section.

The physical adsorption model of a mass exchange between a fluid component, and a solid in porous, and granular materials is based on the classical work of Langmuir (see:

[1], [3] for references). In the original works of Langmuir the theory of adsorption was limited to flat solid surfaces interacting with a gas. However for porous materials whose pores are large - their diameter is greater than app. $500 \text{ \AA} = 50 \text{ nm}$ - one can still rely on the assumption that the influence of the curvature of the surface is small. We discuss the influence of the curvature in the next Subsection. This is why we say that we describe materials with a *large diameter of channels*.

We assume as well that the fluid component consists of two phases. The bulk phase does not exchange mass, and it is solely a carrier of the adsorbate. The second phase - the adsorbate - moves with the velocity of the bulk fluid and its concentration is small

$$c := \frac{\rho_t^A}{\rho_t^F + \rho_t^A} \ll 1, \quad (428)$$

where ρ_t^A, ρ_t^F denote current partial mass densities of the adsorbate, and of the fluid carrier, respectively.

According to Langmuir a transfer of particles of adsorbate from the fluid phase to the surface of the solid depends on the number of available *bare sites* on this surface. The notion of bare sites is introduced in connection with the landscape of interaction energy between adsorbate and the solid skeleton. This landscape depends on a crystallographic or structural symmetry of the skeleton and it has the form of a regular pattern with distributed spots of a maximum interaction energy. On these spots one can expect particles of adsorbate to settle down most frequently. This process is controlled in the first place by the partial pressure of adsorbate in the fluid phase. Certainly there are also particles which desorbate again if they overcome an energy barrier through thermal fluctuations. In the equilibrium one expects these two processes to have the same rate.

Such an adsorption process is called the *monolayer adsorption*. If in a certain domain all available bare sites on the surface of the skeleton are already occupied the adsorption may take place due to interaction of adsorbate particles in their fluid phase and those which are already bound to the skeleton. We deal then with the *multilayer adsorption*. In the case of a small concentration of the fluid adsorbate such exchange of mass between the two phases may be assumed to be less important. We limit attention in these notes solely to the monolayer adsorption model.

In order to construct a continuous model in the spirit of this work we have to construct the mass sources in partial mass balance equations. On the semimacroscopic level (i.e. in the *representative elementary volume* (REV) of a porous or granular material) the normalized fraction of bare sites per unit volume is denoted by $1-x$, i.e. x is the fraction of *occupied sites*. If the area of the internal surface contained in the representative elementary volume is denoted by f_{int} , and the mass of adsorbate per unit area of the internal surface by m^A then the amount of mass which is already adsorbed in the representative elementary volume is in average equal to the product $m^A x f_{int}$.

Let us denote by V the volume of the representative elementary volume. Then the amount of mass of adsorbate transferred in unit time from the fluid phase to the solid skeleton is given by the macroscopic balance relation

$$\hat{\rho}_t^A = -m^A \frac{d(xy)}{dt}, \quad y := \frac{f_{int}}{V}, \quad (429)$$

where $\hat{\rho}_t^A$ denotes the current intensity of mass source per unit time, and unit macroscopic volume.

In order to construct the model we have to specify the rates in this relation. The quantities x, y play in the model the role of additional *microstructural variables*. Field equations for these quantities are assumed to have a form of evolution equations which are specified by relations for the above mentioned rates.

For the rate $\frac{dx}{dt}$ we assume that changes of the fraction x are described by the Langmuir relation

$$\frac{dx}{dt} = a(1-x)p^A - bxe^{-\frac{E_b}{kT}}, \quad (430)$$

where p^A denotes the partial pressure of the adsorbate in the fluid phase, E_b is the energy barrier for particles adsorbed on the solid surface due to the van der Waals interaction forces, and it is assumed to be constant, a , and b are material parameters which within the present model may depend solely on the temperature, k is the Boltzmann constant, and T is the absolute temperature. In the case of full phase equilibrium in which the adsorption rate (the first contribution with coefficient a), and the desorption rate (the second contribution with coefficient b) are equal but of opposite sign we obtain from the equation (430) the following relation for the equilibrium fraction of occupied sites

$$x = x_L := \frac{\frac{p^A}{p_0}}{1 + \frac{p^A}{p_0}}, \quad p_0 := \frac{b}{a}e^{-\frac{E_b}{kT}}. \quad (431)$$

This relation describes the so-called the *Langmuir isotherm*. It begins in the origin $\frac{p^A}{p_0} = 0$ with the zero value of occupied sites and saturates at the value 1 for $\frac{p^A}{p_0} \rightarrow \infty$. At any given partial pressure p^A the fraction x is uniquely determined and it may change its value if we vary the pressure. This corresponds to a slow transition from one thermodynamical equilibrium to another one. In reality such processes are conducted through nonequilibrium states which are described by the rate equation (430) and are connected with the dissipation.

In the mass source (429) we have also another contribution connected with the change of the internal surface. Consequently we must formulate a relation for the rate $\frac{dy}{dt}$. We make the assumption that changes of the internal surface are coupled with dissipative changes of the porosity n which in turn describe relaxation processes of semimacroscopic changes of volume of the skeleton.

First of all let us notice that for sufficiently smooth internal surfaces of porous, and granular materials with a random geometry of pore spaces a change of an average characteristic linear dimension of the internal surface, and this of pores in the elementary representative volume can be assumed to be proportional: $\delta f_{int}^{\frac{1}{2}} \sim \delta(nV)^{\frac{1}{3}}$. Simultaneously dissipative changes of the porosity are given by a source \hat{n} which describes the intensity of these changes per unit time and volume of the porous material. Bearing the above assumption in mind we obtain immediately

$$\frac{1}{y} \frac{dy}{dt} = \varsigma \frac{\hat{n}}{n}, \quad (432)$$

where the proportionality factor ς is assumed to be constant for the purpose of this work.

Obviously in a thermodynamical phase equilibrium $\hat{n} \equiv 0$, and the equilibrium fraction x is connected with the partial pressure p^A through the relation (431). Then the mass source (429) vanishes identically.

The behavior of the continuous model based on the above assumptions has been checked on a simple bench-mark homogeneous problem [62]. It was found that results are indeed qualitatively in agreement with observations.

We present here the set of field equations which covers a much more extensive class of problems. In particular we can describe couplings of adsorption and diffusion as well as we can incorporate boundary conditions on permeable boundaries which are characteristic for the majority of practical problems. According to the above remarks we have to determine the following fields

$$\{\rho_t^S, \rho_t^L, c, \mathbf{v}^S, \mathbf{e}^S, \mathbf{v}^F, n, x, y\}, \quad \rho_t^L := \rho_t^F + \rho_t^A, \quad (433)$$

where the concentration c is defined by (428). The velocity of the third component does not appear because the adsorbate in the fluid phase moves with the same velocity as the other fluid component. Therefore we use only two momentum balance equations, for the skeleton and for both fluid components together.

Field equations follow from three mass balance equations, two momentum balance equations, the balance equation of porosity, integrability condition for the deformation of the skeleton, and two evolution equations for two additional microstructural variables. In the case of small deformations of the skeleton, small changes of the fluid mass density, small concentrations of adsorbate, and small changes of porosity, i.e.

$$\|\mathbf{e}^S\| \ll 1, \quad \left| \frac{\rho_t^L - \rho_0^L}{\rho_0^L} \right| \ll 1, \quad 0 < c \ll 1, \quad |\Delta_n| \ll 1, \quad (434)$$

they have the form

- mass balance

$$\begin{aligned} \frac{\partial \rho_t^S}{\partial t} + \operatorname{div}(\rho_t^S \mathbf{v}^S) &= -\rho_t^L \hat{c}, \quad \frac{\partial \rho_t^L}{\partial t} + \operatorname{div}(\rho_t^L \mathbf{v}^F) = \rho_t^L \hat{c}, \\ \frac{\partial c}{\partial t} + \mathbf{v}^F \cdot \operatorname{grad} c &= (1 - c) \hat{c}, \quad \hat{c} := \frac{\hat{\rho}_t^A}{\rho_t^L} = -\frac{m^A}{\rho_0^L} \frac{d(xy)}{dt}, \end{aligned} \quad (435)$$

- momentum balance

$$\begin{aligned} \frac{\partial \rho_t^L \mathbf{v}^F}{\partial t} + \operatorname{div}(\rho_t^L \mathbf{v}^F \otimes \mathbf{v}^F + p^L \mathbf{1}) + \pi(\mathbf{v}^F - \mathbf{v}^S) &= 0 \\ \rho_t^S \frac{\partial \mathbf{v}^S}{\partial t} &= \operatorname{div} \mathbf{T}^S + \pi(\mathbf{v}^F - \mathbf{v}^S), \end{aligned} \quad (436)$$

- porosity balance

$$\frac{\partial \Delta_n}{\partial t} + \Phi_0 \operatorname{div} (\mathbf{v}^F - \mathbf{v}^S) = -\frac{\Delta_n}{\tau},$$

where

$$\begin{aligned} \mathbf{T}^S &= \mathbf{T}_0^S + \lambda^S \operatorname{tr} \mathbf{e}^S \mathbf{1} + 2\mu^S \mathbf{e}^S + \beta \Delta_n \mathbf{1}, \\ p^L &= p_0^L + \varkappa (\rho_t^L - \rho_0^L) + \beta \Delta_n, \quad p^F = (1 - c) p^L, \quad p^A = c p^L, \end{aligned} \quad (437)$$

with material parameters $\lambda^S, \mu^S, \varkappa, \beta, \pi$ being constant. They depend parametrically on the constant initial porosity n_0 . In addition we have

- integrability condition

$$\frac{\partial \mathbf{e}^S}{\partial t} = \operatorname{sym} \operatorname{grad} \mathbf{v}^S, \quad (438)$$

- evolution equations for microstructural variables

$$\begin{aligned} \frac{d \ln \frac{y}{y_0}}{dt} &= -\varsigma \frac{\Delta_n}{n_E}, \quad y(t=0) = y_0 \equiv \frac{f_{int}(t=0)}{V}, \\ \frac{dx}{dt} &= \frac{1}{\tau_{ad}} \left[(1-x) \frac{c p^L}{p_0} - x \right], \quad x(t=0) = \frac{\frac{c_0 p_0^L}{p_0}}{1 + \frac{c_0 p_0^L}{p_0}}, \\ \tau_{ad} &:= \frac{1}{b} e^{\frac{E_b}{kT}}, \quad c_0 := c(t=0), \end{aligned} \quad (439)$$

Again the material parameters $\varsigma, p_0, \tau_{ad}$ are assumed to be constant.

General results for this system of equations have not been obtained as yet. However some important particular problems have been solved under the assumptions of negligible accelerations, and a negligible explicit time dependence of porosity. Their discussion can be found in the Ph-D Thesis of B. Albers [1]. The most important results have been published [2], [3]. We quote here solely the most important conclusions of these works. The latter assumption yields the following relation for changes of porosity, and the constitutive relations for partial stresses

$$\begin{aligned} \Delta_n &= -\tau \Phi_0 \operatorname{div} (\mathbf{v}^F - \mathbf{v}^S), \\ \mathbf{T}^S &= \mathbf{T}_0^S + \lambda^S \operatorname{tr} \mathbf{e}^S \mathbf{1} + 2\mu^S \mathbf{e}^S - \beta \tau \Phi_0 \operatorname{div} (\mathbf{v}^F - \mathbf{v}^S) \mathbf{1}, \\ p^L &= p_0^L + \varkappa (\rho_t^L - \rho_0^L) - \beta \tau \Phi_0 \operatorname{div} (\mathbf{v}^F - \mathbf{v}^S). \end{aligned} \quad (440)$$

Hence changes of porosity appear in equations of motion in a similar way as contributions of bulk viscosities in mechanics of fluids. Relation (440)₁ allows to eliminate dynamical changes of porosity from field equations.

Let us note that the initial value problem has been already formulated in the above relations. It remains to add boundary conditions. In the two-component case it has the following form

$$(\mathbf{T}^S - p^L \mathbf{1}) \mathbf{n} \big|_{\partial \mathcal{B}_t} = \mathbf{t}_{ext},$$

$$\begin{aligned}\rho^L (\mathbf{v}^F - \mathbf{v}^S) \cdot \mathbf{n} \big|_{\partial \mathcal{B}_t} &= \alpha (p^L - np_{ext}) \big|_{\partial \mathcal{B}_t}, \\ (\mathbf{v}^F - \mathbf{v}^S) - (\mathbf{v}^F - \mathbf{v}^S) \cdot \mathbf{nn} \big|_{\partial \mathcal{B}_t} &= 0.\end{aligned}\tag{441}$$

It is easy to check that these conditions are of the third art.

Such a problem has been analyzed for a 1-D case in the above quoted works of B. Albers. Most important results for applications of the model are connected with couplings of adsorption and diffusion. For instance, it has been shown that the mass source as a function of relative velocity of components possesses a maximum. It is zero for the relative velocity equal to zero and it tends again to zero when this velocity goes to infinity. In the first case the system is in equilibrium and the number of bare sites remains constant and determined by the partial pressure p^A . The internal surface is also constant because the porosity does not change. In the second extreme case relaxation times for internal variables: $\tau_{ad}, \frac{1}{\varsigma}$ are too long for adsorbate to settle down on the skeleton. This indicates the way for an optimal design of filters. Particularly useful is a dependence of the relative velocity from the surface permeability coefficient α because this parameter can be controlled.

11.2 Adsorption for small channel diameter; capillarity

As we have already mentioned processes in materials with the so-called mesopores, i.e. in materials in which the diameter of channels lies in the range $20 - 500 \text{ \AA}$ are connected with the appearance of hysteresis loops in adsorption isotherms. Measurements of their size are used in practical application to find microgeometrical properties of such materials. The reason for the appearance of loops is a capillary condensation. In contrast to the previous case a macroscopic multicomponent model for adsorption with hysteresis has not been constructed as yet.

We proceed to explain the notion of capillary condensation in terms of semimacroscopic description by means of the Kelvin equation.

We begin with mechanical and thermodynamical equilibrium conditions on an interface between two different phases of a liquid. These conditions determine properties of an interface between a fluid and its vapor in the analysis of condensation.

Let us consider a surface in a three-dimensional Euclidean space described by the position vector \mathbf{r}

$$\mathbf{r} = \mathbf{r}(\xi^1, \xi^2), \tag{442}$$

where (ξ^1, ξ^2) are surface coordinates. Base vectors, a normal vector, and the first and second metric tensors of this surface are defined by the relations

$$\begin{aligned}\mathbf{g}_\Delta &:= \frac{\partial \mathbf{r}}{\partial \xi^\Delta}, \quad \mathbf{n} := \frac{\mathbf{g}_1 \times \mathbf{g}_2}{|\mathbf{g}_1 \times \mathbf{g}_2|}, \\ a_{\Delta\Lambda} &:= \mathbf{g}_\Delta \cdot \mathbf{g}_\Lambda, \quad b_{\Delta\Lambda} := \frac{\partial^2 \mathbf{r}}{\partial \xi^\Delta \partial \xi^\Lambda} \cdot \mathbf{n}.\end{aligned}\tag{443}$$

It can be shown that the normal component of the mechanical equilibrium condition on such a surface has the following general form

$$[[\mathbf{Tn}]] \cdot \mathbf{n} = -S^{\Delta\Lambda} b_{\Delta\Lambda}, \tag{444}$$

where \mathbf{T} denotes the Cauchy stress tensor in bulk substances on both sides of the surface, and $S^{\Delta\Lambda}$ are components of the surface stress tensor, both on the level of semimacroscopic description.

In the case of ideal fluids on both sides of the interface which is itself a membrane we have $\mathbf{T} = -p\mathbf{1}$, and $S^{\Delta\Lambda} = \sigma a^{\Delta\Lambda}$, where σ is a *surface tension*. Then relation (444) reduces to the following one

$$p^G - p^F = \sigma \sum_{\alpha=1}^2 \kappa^{(\alpha)} \boldsymbol{\beta}^{(\alpha)} \cdot \boldsymbol{\beta}^{(\alpha)}, \quad (445)$$

where $\kappa^{(\alpha)}$ are eigenvalues, and $\boldsymbol{\beta}^{(\alpha)}$ eigenvectors of the second metric tensor

$$(b_{\Delta\Lambda} - \kappa a_{\Delta\Lambda}) \beta^\Lambda = 0. \quad (446)$$

On the left hand side of (445) we have the difference of pressures between the gaseous phase, and the fluid phase, respectively.

In addition to the mechanical equilibrium condition (445) an equilibrium on the interface is determined by the thermodynamical condition of equal chemical potentials (Gibbs free energies) of both phases

$$\mu^G(T^G, p^G) = \mu^F(T^F, p^F), \quad (447)$$

where p^G, p^F are pressures in the gaseous phase, and in the fluid phase, respectively. We assume the temperatures to be equal and constant: $T^G = T^F = T = \text{const}$.

We apply the above conditions to a small change of the equilibrium. We have then

$$d\mu^G \equiv V^G dp^G = d\mu^F \equiv V^F dp^F, \quad (448)$$

and, hence, by substitution in (445)

$$dp^G - dp^F = \left(1 - \frac{V^G}{V^F}\right) dp^G \approx -\frac{V^G}{V^F} dp^G = \sigma d\left(\frac{1}{r_1} + \frac{1}{r_2}\right), \quad (449)$$

where $\frac{1}{r_1}, \frac{1}{r_2}$ denote the main curvatures. It was assumed that the volume of fluid phase is much smaller than this of the gaseous phase: $V^F \ll V^G$ and that the surface tension σ is constant. For ideal gases we have

$$\frac{RT}{V^F} d \ln p^G = -\sigma d\left(\frac{1}{r_1} + \frac{1}{r_2}\right), \quad (450)$$

where R is the gas constant.

Integration of this relation yields the *Kelvin relation*

$$\ln \frac{p}{p_0} = -\frac{\sigma V^F}{RT} \left(\frac{1}{r_1} + \frac{1}{r_2}\right), \quad (451)$$

in which p_0 is the integration constant which we identify with the saturation pressure.

We demonstrate the properties described by relation (451) on a simple example of a cylinder open on both ends.

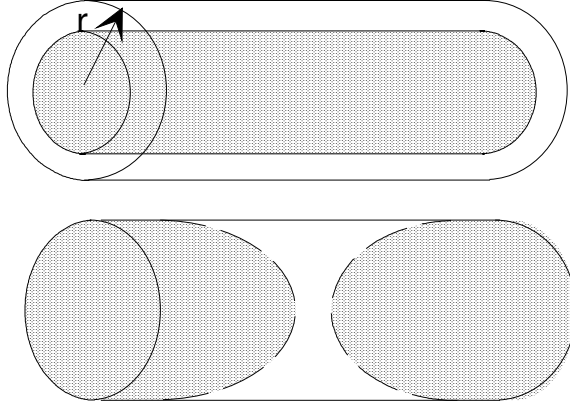


Figure 14: *Scheme of capillary condensation and evaporation in a cylinder*

Imagine a carrier of adsorbate filling the cylinder in the initial state with the partial pressure p of the adsorbate given by (451) for $r_1 = r, r_2 = \infty$, where r denotes the radius of the cylinder (Figure 14). The process of condensation may occur below the saturation pressure p_0 if there is a thin film of adsorbate on the internal wall of the cylinder. This yields the existence of a surface tension and, according to Kelvin formula, the partial pressure p at which condensation occurs is lower than p_0 . Once the nucleation on this thin meniscus begins the partial pressure of adsorbate decreases and this yields a decrement of the radius of the cylindrical space still filled with the gas (upper part of Fig. 14). This process is, of course, unstable and it means that it terminates when the cylinder contains solely a condensed fluid form of the adsorbate.

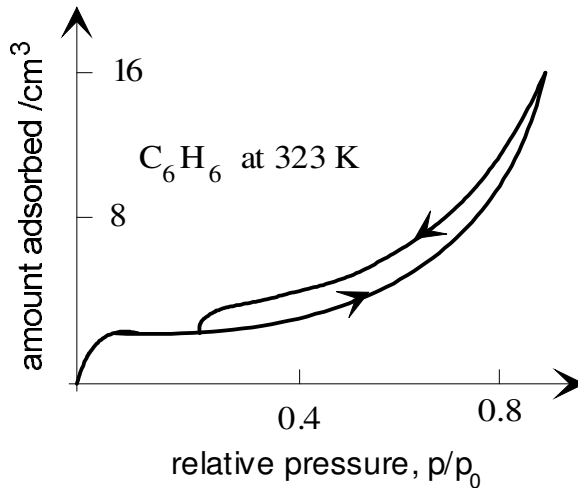


Figure 15: *Condensation and evaporation on a sodium-rich montmorillonite [25]*

In Figure 15 it corresponds to the lower curve of the hysteresis loop reflecting the process of condensation. On the other hand the evaporation does not require a nucleation. It proceeds from the heads of the cylinder by moving hemispherical meniscus from both ends

of the cylinder to its interior (lower part of Fig. 14). In this process $r_1 = r_2 = r$, which means that the partial pressure is lower than in the case of condensation. Consequently we observe a hysteresis shown on the example of Figure 15.

Processes in channels of real materials with mesopores are similar to this described in the above example. However the appearance of hysteresis loops is connected with various geometrical properties and their macroscopic description usually requires essential modifications of the model for particular materials.

12 Perspectives

Continuum multicomponent theories of porous materials which we presented in these notes are still in a rather early stage of development. They require essential physical modifications as well as investigations of their mathematical properties. Let us list a few most important questions which should be answered in near future.

1. *Nonisothermal processes.*

We have mentioned already problems arising in connection with a macroscopic definition of thermodynamical temperature or multiple temperatures. There may be a way out of this problem if we work with some alternative notion such as an internal partial energy itself. One of the problems which can be solved easily in such a formulation is a transfer of energy by convection (relative motion) with negligibly small contributions of heat conduction. Such a problem may clear some couplings of diffusion and of a heterogeneous temperature distribution. But the main question of measurable thermal quantities cannot be answered in this way.

2. *Entropy condition and entropy flux.*

These problems arise in general thermodynamical considerations as well as in connection with the selection criterion for weak solutions, satisfying Rankine-Hugoniot conditions.

All thermodynamical results which were presented in these notes and which led to essential constitutive restrictions were based on the assumptions that the partial heat fluxes and entropy fluxes are proportional to each other with the inverse of the absolute temperature as the proportionality factor, and that processes are isothermal. Such assumptions are too restrictive for both thermodynamical purposes and for a theory of shock waves in porous materials.

3. *Nonelastic and nonlinear elastic behavior of the skeleton.*

These problems are primarily connected with practical applications of theories of porous materials in soil mechanics of clays, thermomechanics of sponges and other filters undergoing large deformations, etc. The way seems to be straightforward because there exist already one-component models for such a behavior, and methods of extended thermodynamics seem to be appropriate to incorporate those results in the scheme of multicomponent models.

4. *Extensions of microstructure and multiscaling problems.*

Some of these problems are being approached already. This concerns particularly systems with a double porosity, materials with a heterogeneous initial porosity, but also problems connected with mass exchange which require additional microstructural variables. A big open question is a transition between various levels of observation and averaging techniques in the derivation of macrosopic constitutive laws from microscopic and semimacroscopic relations.

5. *Chemical reactions and phase transitions. Capillarity and hysteresis.*

The first group, chemical reactions, can be approached in a way suggested by classical continuum theories of mixtures. The condition for a successful construction of such models is an answer on the first question listed above.

On the other hand, problems connected with the description of phase transitions, such as condensation and evaporation, capillarity, melting etc. follow primarily from the lack of transitions between various scales of description. A commonly used mathematical model of capillarity in porous materials which follows from the diffusion-reaction equations is physically very doubtful due to physical notions appearing in macroscopic description (such as pressure, saturation pressure, temperature) which are taken over from semimacroscopic models without any justification by, for example, averaging procedures.

6. *Nonlinear waves in porous materials.*

There exists no systematic research of this question. The reason is that nonlinear multicomponent models are not sufficiently developed as yet. Apart from nonlinearities connected with constitutive laws for the skeleton which we have mentioned above, laws for fluid components should go beyond simple linear compressible and ideal fluids. Such problems arise, for instance, in modelling of fluids containing bubbles of vapor. Analysis should concern not only strong discontinuity waves but also, due to their practical importance, surface waves. This research has been already initiated.

7. *Weak solutions, numerical methods.*

There is a considerable progress in recent years within the second part of this problem. Some multicomponent models of porous materials, particularly these based on the assumption of incompressibility and commonly used in soil mechanics, have an extensive numerical literature. We shall not quote it here because it concerns a different class of models. For nonlinear models of compressible components as presented in these notes, there exist only few numerical works.

From the point of view of analytical properties of these models first steps have been made and some of the results were indicated in this work. From the purely mathematical standpoint properties of weak solutions for the model presented in these notes are not available as yet.

8. Granular materials, unilateral constraints.

We have mentioned that certain classes of processes in granular materials can be described by continuous models identical with those for porous materials. However a natural condition which should be incorporated into constitutive models of granular materials not carrying tension has never been investigated with a tacit assumption that solutions should not be extended so far. A proper constitutive model should rely on additional mechanical unilateral constraints.

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