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On thermodynamic modeling and the role of the second law of thermodynamics in geophysics

Krzysztof Wilmanski

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Weierstrass Institute
for Applied Analysis
and Stochastics
Mohrenstr. 39
10117 Berlin
Germany
E-Mail: wilmansk@wias-berlin.de

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Edited by
Weierstraß-Institut für Angewandte Analysis und Stochastik (WIAS)
Mohrenstraße 39
D — 10117 Berlin
Germany

Fax: + 49 30 2044975
E-Mail: preprint@wias-berlin.de
World Wide Web: http://www.wias-berlin.de/

Abstract

The article contains a brief review of elements of thermodynamic modeling in theoretical geophysics. We motivate the existence of the second law of thermodynamics in macroscopic theoretical physics and demonstrate its evaluation. In particular we show its consequences in the construction of constitutive laws for a two-component poroelastic medium. This construction is also related to microstructural properties verified by means of the second law.

1 Introduction[1]

The second law of thermodynamics as a fundamental principle of macroscopic physics has a rather untypical history. It has been discovered by an engineer for purely practical purposes and, as such, has not been questioned. However its justification within theoretical physics led to vehement discussions with, sometimes tragic consequences such as the suicide of Boltzmann. It was related to pessimistic philosophical considerations (the ”entropic death” of the universe), enthusiastic expectations of some scientists that it may give them a tool to construct automatically models for complicated processes, etc. During the last thirty years the situation became normal – the second law of thermodynamics is now one of basic principles in the construction of macroscopic models but it is, of course, not a panacea for all our problems. Very often we can solely find some restrictions in form of inequalities but not prescriptions for determining parameters. A prominent example of such a thermodynamic result is the inequality restricting the coefficient of thermal expansion α

$$0 \leq \alpha \leq \frac{1}{vT} c_p \kappa,$$

where v, T denote the specific volume and the absolute temperature, respectively, c_p is the specific heat under constant pressure and κ is the compressibility of the fluid. This inequality says that one cannot construct a model of a fluid by assuming incompressibility ($\kappa = 0$) and simultaneously admitting the thermal expansion ($\alpha > 0$) which is, however, done in the so-called Boussinesq approximation [1] important for the stability analysis of fluids.

In this work we want to show some facets of the second law of thermodynamics within theoretical geophysics. We begin with a motivation of the existence of this law. To this aim we present a Gedankenexperiment whose origin goes back to

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[1] This article contains a comprehensive presentation of my lectures during the series of conferences GEOMATH organized by Prof. D. Kolymbas (Innsbruck).

Ehrenfest. This experiment was designed to reproduce considerations of Boltzmann in which he was justifying the existence of macroscopic irreversibility derived from a microscopic reversible model (the famous H-Theorem).

In the third section I present two simple examples of application of the second law of thermodynamics. The first example stems from soil mechanics and it is related to the evaluation of macroscopic material parameters by means of some microscopic data. This evaluation relies on certain assumptions concerning properties of the surface of contact between two different media. Using the second law of thermodynamics we demonstrate limitations on the practical applicability of classical results. The second example illustrates two different ways of exploitation of the second law. We show that they yield the same results. The most complicated technical part of the work is contained in section 4. We show some consequences of the second law for the construction of a nonlinear two-component (hence – fully saturated) model of poroelastic materials. The aim of this section is twofold. We present the technique which is used in the evaluation of the second law in continuum physics, and, simultaneously, we obtain the thermodynamic framework for the most popular model of porous materials used in acoustics of these media – the Biot model. Finally in the fifth section we discuss some problems of construction of macroscopic parameters of a linear model by means of the transition from the microscopic description. In this example we show the limitations imposed on such a transition by thermodynamic conditions applied to the microstructure and discussed in the example of section 2.

References to original works are rather scarce. I am quoting some more or less standard books and solely as examples some papers. There exists a vast literature on the subject and it would be irrational to account properly for all contributions in the article of this size.

2 Motivation

The second law of thermodynamics has a somewhat mysterious ring among people who do not work professionally with its applications. For this reason I begin this work with a brief motivation for the existence of this principle of macroscopic physics.

I proceed to describe one of the most impressive models or Gedankenexperiments demonstrating the source of irreversibility of macroscopic processes, and, consequently, the origin of the second law of thermodynamics. This model which I quoted in my book [2] goes back to Ehrenfest but it has been designed and discussed in many details in an almost unknown book of Mark Kac [3].

Let us consider a circle on which we locate n points in equal distance from each other. They are vertices of a polygon. A set S of m vertices is chosen, and these points have a special property which we define further. In each point n we locate a ball which may be either white or black. Now we define the dynamics of this model. We move all balls simultaneously in – say – anticlockwise direction in discrete time steps Δt. In each step balls which were located in points of the set S change the colour. All other balls do not change their colour. For simplicity we assume that at the initial instant of time $t = 0$ all balls are black. However this assumption is immaterial for properties of the dynamics of the system. It is intuitively clear that after sufficiently many steps and for the points of the set S randomly distributed on the circle approximately a half of the balls will be white and the other half black. Simultaneously if we rotate the system by the angle 4π it returns to its initial state – each ball changes its colour even times $2m$, and hence it will have again the initial colour, i.e. sufficiently long processes are periodic. Moreover processes are reversible, i.e. they are invariant with respect to the transformation $t \to -t$. Such a transformation means that we have to rotate the system in the clockwise direction. But this leads to the initial state again if we make sufficiently many steps. In addition the clockwise rotation describes exactly the same processes as the anticlockwise rotations – they become identical by renaming black balls to white and *vice versa*.

In order to describe this model analytically we denote by $N_b(t)$ the number of black balls, and by $N_w(t)$ the number of white balls. Initially $N_b(t = 0) = n$. Let $N_b(S,t)$, and $N_w(S,t)$ denote the number of black and white balls, respectively, occupying points of the set S. We have the following conservation laws

$$N_b(t) + N_w(t) = n, \quad N_b(S,t) + N_w(S,t) = m. \tag{1}$$

Simultaneously the following relations describe the discrete dynamics of the model. The number of black balls after the time step $t \to t + \Delta t$ is

$$N_b(t + \Delta t) = N_b(t) + N_w(S,t) - N_b(S,t), \tag{2}$$

because the balls occupying points of the set S in the instant of time t have changed the colour in this step. Similarly for the white balls we have

$$N_w(t + \Delta t) = N_w(t) + N_b(S,t) - N_w(S,t). \tag{3}$$

Now we use the **assumption** on random distribution of points of the set S among all points on the circle. After sufficiently long time lapse from the beginning of motion we expect that the fraction of black balls in the set S will be the same as the fraction of these balls in the set of all balls: $\frac{N_b(S,t)}{m} = \frac{N_b(t)}{n}$. The same concerns the white balls. Hence we have

$$N_b(S,t) = \frac{m}{n} N_b(t), \quad N_w(S,t) = \frac{m}{n} N_w(t). \tag{4}$$

The set of equations describing our model is now complete and we can proceed to its analysis.

If we subtract equations (2), (3) and substitute the assumption (4) the following equation for the increments follows

$$N_b(t + \Delta t) - N_w(t + \Delta t) = \left(1 - 2\frac{m}{n}\right) \left[N_b(t) - N_w(t)\right]. \tag{5}$$

This simple equation in finite differences can be immediately solved and we obtain

$$\frac{N_b(t) - N_w(t)}{n} = \frac{N_b(0) - N_w(0)}{n} \left(1 - 2\frac{m}{n}\right)^t . \tag{6}$$

The solution determines the surplus of black balls over the white balls at any instant of time t. As $N_w(0) = 0$ we can write it also in the following form

$$N_b(t) + N_w(t) = n \Longrightarrow N_b(t) = \frac{n}{2}\left[1 + \left(1 - 2\frac{m}{n}\right)^t\right] . \tag{7}$$

Reasonable values (existence of solutions under the assumption (4)!) follow under the assumption that the number m of points in the set S is smaller than $\frac{n}{2}$. Then the surplus of black balls over the white balls will decrease and in the limit $t \to \infty$ it will be zero, i.e. a half of the balls will be black and another half – white. This agrees with our intuition. However it contradicts the periodicity of the system!

In the above considerations there is only one assumption. It is described by relations (4). This assumption is an analogon of the famous "Stoßzahlansatz" which Boltzmann made in his derivation of the kinetic theory of gases. The whole construction presented above is a very simplified version of the reasoning of Boltzmann and the conclusion following from the relation (6) corresponds to his H-theorem. This theorem is the prototype of the modern second law of thermodynamics. Simultaneously the assumption (4) is a stochastic element of the model and such a feature possess all our macroscopic models in physics.

In the situation of such a contradiction we either have to change the model or we have to apply a different interpretation of results. As both the assumption and the result seem to correspond well with our intuition we try to apply a different interpretation.

If the number of balls corresponded to the number of particles of a real substance (say a gas such as the air) then in typical conditions on the earth it would be of the order $\sim 10^{23}$ (Avogadro number). For the time step $\Delta t = 10^{-2}$ sec this would mean that the system would return to its initial state (reccurence time) after $2 \cdot 10^{21}$ seconds, i.e. after approximately $6 \cdot 10^{13}$ years. This is more than 1000 times longer than the lifetime of the universe since the big bang! Consequently we may consider the solution (6) to be a good approximation if the time lapse from the beginning of the process is neither too long nor too short.

Certainly the above very simple model cannot give even a hint whether real processes in nature are reversible or even periodic in a sense of very long observation times. However it justifies the statement that a stochastic element involved in any description of macroscopic processes in realistic times of observation yields **irreversibility**. This is also the reasonable approach in our macroscopic theories of geophysical systems.

The theory constructed by Boltzmann yields a criterion for the time behaviour described by such solutions as (6). Namely for isolated systems, i.e. systems which do not interact with the external world, one can introduce a function which depends on parameters of the system and which grows in time until it reaches a limit state – the thermodynamic equilibrium – and then remains constant. We denote this function by H and call it the **entropy function**. We have then

$$\frac{dH}{dt} \geq 0, \tag{8}$$

in each instant of time for real processes, i.e. for solutions of equations describing the system. In a different way without refering to stochastic arguments unknown at that time such a criterion for admissibility of models has been introduced by Rudolf Clausius in 1850 who invented the name entropy and by William Thomson Kelvin in 1851 who called it the degradation of energy. Both were motivated by the famous work of Nicolas Carnot on the efficiency of heat engines published in 1824.

The inequality (8) which is predesignated to lead to the second law of thermodynamics possesses already the most important feature of this law. It predicts the **relaxation** of isolated systems to the thermodynamic equilibrium in which $\frac{dH}{dt} = 0$. If the system is not isolated from the external world there exists an exchange of mass, momentum, energy etc. between the system and the rest of the world which may contribute to changes of H. Then we have to correct the inequality (8) by a supply term Φ describing the amount of the entropy H carried into the system from the external world per unit time

$$\frac{dH}{dt} + \Phi \geq 0. \tag{9}$$

As the entropy itself, it depends on parameters of the system. In the next section we show some simple examples of such a supply.

The entropy function H and its supply Φ are defined for the whole system. However we can extend this statement requiring that this law must hold as well for some subsystems defined, for instance, on a part $\mathcal{P}$ of the domain $\mathcal{B}$ occupied by the system in the three-dimensional Euclidean space of motion. In such cases, most common in practical applications, it is also required that the entropy is an **additive** function, i.e for two separate subsystems $\mathcal{P}_1, \mathcal{P}_2$, with $\mathcal{P}_1 \cap \mathcal{P}_2 = \emptyset$, the entropy of the sum of these two systems is equal to the sum of entropies: $H(\mathcal{P}_1 \cup \mathcal{P}_2) = H(\mathcal{P}_1) + H(\mathcal{P}_2)$. Certain additional mathematical assumptions which are the same as in any continuum model (e.g. [4]) lead then to the existence of the entropy density η which satisfies the following relations

$$H(\mathcal{P}) = \int_{\mathcal{P}} \rho\eta dV, \quad \frac{d}{dt}\int_{\mathcal{P}} \rho\eta dV + \underbrace{\oint_{\partial\mathcal{P}} \mathbf{h}\cdot\mathbf{n} dS - \int_{\mathcal{P}} \rho s dV}_{=\Phi} \geq 0. \tag{10}$$

In these relations η is called the specific entropy, ρ is the mass density of the system, i.e. $M(\mathcal{P}) = \int_{\mathcal{P}} \rho dV$ is the mass of $\mathcal{P}$, $\mathbf{h}$ denotes the flux of entropy through the unit surface and in the unit time, s is the so-called entropy radiation to the external world, and $\mathbf{n}$ denotes a unit normal vector of the surface (boundary) $\partial\mathcal{P}$ of the system. This inequality can be written in the local form by means of the Stokes theorem on the transformation of surface integrals for closed surfaces into volume integrals

$$\frac{\partial(\rho\eta)}{\partial t} + \operatorname{div}(\rho\eta\mathbf{v} + \mathbf{h}) - \rho s \geq 0, \tag{11}$$

where $\mathbf{v}$ is the velocity of particles of the system. It must hold **for all real processes** in the system in almost all points of the set $\mathcal{B}$. The last condition means that the local form (11) can be violated in single points, on some lines or surfaces of the system for which, however, the global form (10) still should be true in the limit sense.

The relation (11) – the so-called entropy inequality – is the modern form of the **second law of thermodynamics for continua**.

Further in this work we show how this condition can be evaluated in the construction of various models in geophysics. In the next section we discuss first two very simple examples which have, however, a certain practical bearing.

3 Two simple examples of evaluation of the second law

We begin the demonstration of consequences of the second law of thermodynamics with an example appearing in procedures of transformation of data for real granular materials into a macroscopic multicomponent model. We return to this problem in its full generality further in this work. The purpose of the present analysis is solely to derive restrictions for the microscopic model. We describe it for the so-called **unjacketed** test of a two-component granular material (e.g. [5, 6])[2]. In this model we consider homogeneous, quasistatic processes in a heap of a compressible granular material immersed within a fluid. On the upper surface of the fluid the pressure p' is acting. We assume that the system preserves a constant temperature $T = T_0$ (isothermal processes).

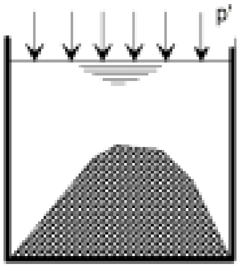

Figure 1: *Scheme of the unjacketed test*

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[2] I am grateful to Dr. W. Dreyer (WIAS, Berlin) for suggesting this problem.

Processes in this system are described by means of the following variables: M^S – the mass of the solid granular material, M_i^F – the mass of the fluid inside the pores of the granular material, M_e^F – the mass of the fluid outside the heap, V^S – the volume of the solid granular material, V_i^F – the volume of the fluid inside the heap, V_e^F – the volume of the fluid outside the heap. We call the variables $\left\{M^S, M_i^F, M_e^F, V^S, V_i^F, V_e^F, T_0\right\}$ the process parameters. The purpose is to describe conditions between the heap and the exterior.

We proceed to exploit two laws of thermodynamics: the **conservation of energy** and the **second law of thermodynamics**. Let us denote by $\dot{Q}$ the amount of the energy which is carried into the system in a nonmechanical form (heat supply) from the external world in the unit time. Then the change of the energy E in the quasistatic process (the influence of the kinetic energy is neglected!) is described by the following first law of thermodynamics (conservation of energy)

$$\frac{dE}{dt} + \dot{Q} + \underbrace{p' \frac{d}{dt}\left(V^S + V_i^F + V_e^F\right)}_{\text{mechanicalworking}} = 0, \tag{12}$$

The heat supply $\dot{Q}$ is necessary for processes to pertain to isothermal conditions.

The **second law of thermodynamics** has the following form

$$\frac{dH}{dt} + \frac{\dot{Q}}{T_0} \geq 0, \tag{13}$$

where the form of the entropy supply $\Phi = \dfrac{\dot{Q}}{T_0}$ follows from the original considerations of Carnot and Kelvin. We show later that this is not always an appropriate form of such a relation.

Substitution of (12) in (13) yields

$$\frac{d\Psi}{dt} + p' \frac{d}{dt}\left(V^S + V_i^F + V_e^F\right) \leq 0, \tag{14}$$

where

$$\Psi := E - T_0 H, \tag{15}$$

is the so-called Helmholtz free energy. As the energy E and the entropy H it is assumed to be additive, i.e. it is in our example the sum of the free energy of the solid, and of the two parts of the fluid.

We make now the **constitutive assumption** which defines materials involved in the process. As the free energies possess densities this assumption shall be made for densities in a homogeneous process. Namely

$$\Psi = M^S \psi^S\left(T_0, \frac{V^S}{M^S}\right) + M_i^F \psi^F\left(T_0, \frac{V_i^F}{M_i^F}\right) + M_e^F \psi^F\left(T_0, \frac{V_e^F}{M_e^F}\right), \tag{16}$$

i.e. we assume that the densities of free energy depend on the temperature (a constant in our case), and on the specific volume $\frac{V}{M}$ for each component. The latter is, of course, identical with the inverse of the mass density, and the specific volumes have been chosen solely for historical reasons. Both fluid contributions contain the same function $\psi^F(T_0,\cdot)$ because it is **the same** fluid in the heap and outside of the heap. Now it follows from (14) by means of the chain rule of differentiation

$$\begin{aligned}
&\left(\psi^S - \psi^{S\prime}\frac{V^S}{M^S}\right)\frac{dM^S}{dt} + \left(\psi_i^F - \psi_i^{F\prime}\frac{V_i^F}{M_i^F}\right)\frac{dM_i^F}{dt} + \left(\psi_e^F - \psi_e^{F\prime}\frac{V_e^F}{M_e^F}\right)\frac{dM_e^F}{dt} + \\
&\quad + \left(p' + \psi^{S\prime}\right)\frac{dV^S}{dt} + \left(p' + \psi_i^{F\prime}\right)\frac{dV_i^F}{dt} + \left(p' + \psi_e^{F\prime}\right)\frac{dV_e^F}{dt} \leq 0,
\end{aligned} \tag{17}$$

where the indices i, e denote the evaluation at the corresponding values of the arguments, and the prime denotes the derivative with respect to the specific volume. This inequality must be satisfied for all real processes in our system. However real processes must satisfy the following constraints

$$M^S = \text{const.}, \quad M_i^F + M_e^F = \text{const.}, \tag{18}$$

which are, of course, the mass conservation laws. Otherwise the values of time derivatives in (17) are arbitrary. It means that the inequality can be satisfied solely in the case when the coefficients of these derivatives vanish identically. We obtain

$$\begin{aligned}
&p^S := -\frac{d\psi^S}{d\left(\frac{V^S}{M^S}\right)} = p', \quad p_i^F := -\left.\frac{d\psi^F}{d\left(\frac{V^F}{M^F}\right)}\right|_{\frac{V^F}{M^F}=\frac{V_i^F}{M_i^F}} = p', \\
&p_e^F := -\left.\frac{d\psi^F}{d\left(\frac{V^F}{M^F}\right)}\right|_{\frac{V^F}{M^F}=\frac{V_e^F}{M_e^F}} = p',
\end{aligned} \tag{19}$$

$$\psi_i^F - \psi_i^{F\prime}\frac{V_i^F}{M_i^F} = \psi_e^F - \psi_e^{F\prime}\frac{V_e^F}{M_e^F} \Longrightarrow \underline{\psi_i^F + p_i^F\frac{V_i^F}{M_i^F} = \psi_e^F + p_e^F\frac{V_e^F}{M_e^F}},$$

where p^S is the pressure in the solid, p_i^F – pressure in the fluid inside the heap (**pore pressure**), p_e^F – pressure in the fluid outside the heap.

The last condition contains the combination of the Helmholtz free energy with the pressure contribution. This combination is called the **free enthalpy**. The condition means that this quantity must be the same in the fluid inside of the heap and outside of the heap (continuity across the interface between the two parts). Simultaneously the first three relations reduce the number of necessary constitutive relations from three to two for the two Helmholtz free energies. Let us note that the above relations reduce the second law to the identity which means that the system is in thermodynamic equilibrium.

According to the above relations we can make still a further simplification provided constitutive relations are monotone with respect to the specific volume[3]

$$p_i^F = p_e^F \equiv p' \quad \Longrightarrow \quad \frac{V_i^F}{M_i^F} = \frac{V_e^F}{M_e^F}. \tag{20}$$

Hence the mass density of the fluid is the same inside and outside of the heap and the condition for the enthalpy becomes trivial.

The above considerations yield rather trivial results anticipated in previous works on this subject. However they expose simplifications which must be made in order to obtain the condition (20). We list the most important of them.

- The solid granular material must react on volume changes in an elastic way, i.e. its pressure is dependent solely on changes of the mass density $\frac{M^S}{V^S}$. For instance we have not incorporated any viscoplastic changes of the volume;
- The fluid is ideal, i.e. its pressure depends also solely on changes of mass density. We have neglected, for instance, viscous properties or friction between the fluid in the heap and the grains.

Viscoplastic deformations of the solid and viscous properties of the fluid would require a considerable modification of the second law (14).

- There is no influence of capillary forces which would have to appear in the energy balance through an additional term defined on the contact surface (interface) between the fluid in the heap and outside of the heap;
- All processes are homogeneous, i.e we neglect, for example, the pattern formation (e.g. a heterogeneous deformation in the form of layered structure) in the heap;
- The heap is fully saturated by the fluid;
- There is no mass exchange between the solid and the fluid, and phase transformations (e.g. evaporation and condensation) are excluded.

Certainly one can add more items to this list.

The results for this simple example show the limitations which are imposed on the classical Gassmann relations between microscopic and macroscopic properties of granular materials (see: Sect. 5 for the presentation of this problem), and, simultaneously, they indicate the way in which these relations can be improved. Clearly, if

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[3] Such a relation would not hold, for instance, in the case of hysteresis (i.e. materials with a phase transformation) in which at least two different mass densities correspond to the same pressure.

any of the above listed issues will be corrected the continutity of the pressure in the fluid (20) must be replaced by the continuity of the enthalpy $(19)_3$.

We proceed to discuss the second simple example. We investigate thermodynamic limitations for the so-called **rigid heat conductor**. It is a solid in which solely the temperature field $T(\mathbf{x},t)$ determines processes. The field equation for this field follows from the energy conservation law. In the local form it is as follows

$$\rho\frac{\partial\varepsilon}{\partial t}+\operatorname{div}\mathbf{q}=\rho r, \tag{21}$$

where ρ is the constant mass density ε denotes the specific internal energy per unit mass $\mathbf{q}$ is the so-called heat flux vector, and r – radiation density. In a further thermodynamic analysis we neglect the last contribution because it is controlled by external agents and, for this reason, can be switched off without any influence on properties of the material. In order to transform the equation (21) into the field equation for the temperature T we have to specify the dependence of ε and $\mathbf{q}$ on the temperature and its derivatives. In the classical case it is assumed that the following simplified caloric relation for the specific energy and the Fourier relation for the heat flux, respectively, hold true

$$\varepsilon=\varepsilon(T), \quad \mathbf{q}=-K(T)\,\mathbf{g}, \quad \mathbf{g}:=\operatorname{grad}T. \tag{22}$$

Substitution in (21) yields the classical heat conduction equation

$$\rho c_v\frac{\partial T}{\partial t}=\operatorname{div}\left(K\operatorname{grad}T\right)\mathbf{q}+\rho r, \quad c_v:=\frac{d\varepsilon}{dT}. \tag{23}$$

We evaluate the second law for a slightly more general case. Namely we assume that the specific energy ε, the heat flux $\mathbf{q}$, the specific entropy η, and the entropy flux $\mathbf{h}$, are functions of the temeperature T and its gradient $\operatorname{grad}T$. In addition we assume this system to be isotropic. We specify consequences of the latter assumption later. Then the energy balance (21) has the form

$$\rho\left(\frac{\partial\varepsilon}{\partial T}\frac{\partial T}{\partial t}+\frac{\partial\varepsilon}{\partial\mathbf{g}}\cdot\frac{\partial\mathbf{g}}{\partial t}\right)+\frac{\partial\mathbf{q}}{\partial T}\cdot\mathbf{g}+\frac{\partial\mathbf{q}}{\partial\mathbf{g}}\cdot\left(\operatorname{grad}\mathbf{g}\right)=0, \tag{24}$$

and the entropy inequality (11) is as follows

$$\rho\left(\frac{\partial\eta}{\partial T}\frac{\partial T}{\partial t}+\frac{\partial\eta}{\partial\mathbf{g}}\cdot\frac{\partial\mathbf{g}}{\partial t}\right)+\frac{\partial\mathbf{h}}{\partial T}\cdot\mathbf{g}+\frac{\partial\mathbf{h}}{\partial\mathbf{g}}\cdot\left(\operatorname{grad}\mathbf{g}\right)\geq 0. \tag{25}$$

We have to evaluate the above inequality provided the field T satisfies its field equation, i.e. it must satisfy the above energy conservation law. This condition is a **constraint** on the class of admissible solutions of the inequality. Such constraints are eliminated in modern thermodynamics by means of Lagrange multipliers. We discuss this issue in some details further in this work. However, in order to show that the choice of a method for the evaluation of the second law of thermodynamics is solely a matter of convenience we proceed here by means of a direct method and then we show that the results are the same.

Namely among all possible local values of derivatives of the temperature the derivative, say, with respect to time can be calculated from the energy conservation provided the coefficient $c_v = \frac{\partial \varepsilon}{\partial T}$ is different from zero. This shall be so assumed. Then

$$\frac{\partial T}{\partial t} = -\left(\frac{\partial \varepsilon}{\partial T}\right)^{-1}\left\{\left[\frac{\partial \varepsilon}{\partial \mathbf{g}} \cdot \frac{\partial \mathbf{g}}{\partial t}\right] - \frac{1}{\rho}\left[\frac{\partial \mathbf{q}}{\partial T} \cdot \mathbf{g} + \frac{\partial \mathbf{q}}{\partial \mathbf{g}} \cdot (\operatorname{grad} \mathbf{g})\right]\right\}. \tag{26}$$

On the right hand side of this relation derivatives can be chosen arbitrarily because no other field equation appears in this model. We substitute this result in the entropy inequality (25). We obtain then

$$\rho\left[\Lambda \frac{\partial \varepsilon}{\partial \mathbf{g}} - \frac{\partial \eta}{\partial \mathbf{g}}\right] \cdot \frac{\partial \mathbf{g}}{\partial t} + \left[\Lambda \frac{\partial \mathbf{q}}{\partial T} - \frac{\partial \mathbf{h}}{\partial T}\right] \cdot \mathbf{g} +$$

$$+\left[\Lambda \frac{\partial \mathbf{q}}{\partial \mathbf{g}} - \frac{\partial \mathbf{h}}{\partial \mathbf{g}}\right] \cdot \operatorname{grad} \mathbf{g} \leq 0, \quad \Lambda := \left(\frac{\partial \eta}{\partial T}\right)\left(\frac{\partial \varepsilon}{\partial T}\right)^{-1}. \tag{27}$$

As the derivatives $\frac{\partial \mathbf{g}}{\partial t}$, $\operatorname{grad} \mathbf{g}$ contribute in linear way to this inequality and they can be chosen arbitrary their coefficients must vanish. Hence we obtain

$$\Lambda \frac{\partial \varepsilon}{\partial \mathbf{g}} - \frac{\partial \eta}{\partial \mathbf{g}} = 0, \quad \operatorname{sym}\left(\Lambda \frac{\partial \mathbf{q}}{\partial \mathbf{g}} - \frac{\partial \mathbf{h}}{\partial \mathbf{g}}\right) = 0. \tag{28}$$

We proceed to use the assumption of isotropy. Then the vector functions $\mathbf{q}, \mathbf{h}$ must depend on the vector argument in the following way

$$\mathbf{q} = -K\left(T, g^2\right)\mathbf{g}, \quad \mathbf{h} = -H\left(T, g^2\right)\mathbf{g}, \quad g^2 := \mathbf{g} \cdot \mathbf{g}. \tag{29}$$

Consequently the second relation (28) can be written in the form

$$-(\Lambda K - H)\mathbf{1} - 2\left(\Lambda \frac{\partial K}{\partial g^2} - \frac{\partial H}{\partial g^2}\right)\mathbf{g} \otimes \mathbf{g} = 0. \tag{30}$$

Separation of the deviatoric and spherical parts in this relation yields

$$\Lambda K - H = 0, \quad \Lambda \frac{\partial K}{\partial g^2} - \frac{\partial H}{\partial g^2} = 0. \tag{31}$$

Now the substitution of the first identity in the second one yields

$$\frac{\partial \Lambda}{\partial g^2} = 0 \quad \Longrightarrow \quad \frac{\partial \eta}{\partial T} = \Lambda(T)\frac{\partial \varepsilon}{\partial T} \quad \Longrightarrow \quad \Lambda = \frac{1}{T}, \tag{32}$$

where the classical Gibbs thermostatics (i.e. Gibbs equation in the thermodynamic equilibrium: $d\eta = \frac{1}{T}\left(d\varepsilon + pdV\right)$, $dV \equiv 0$, V - volume; e.g. see: [7]) has been used in the last implication. This yields

$$H = \frac{1}{T}K \quad \Longrightarrow \quad \mathbf{h} = \frac{1}{T}\mathbf{q}. \tag{33}$$

We have anticipated this result in the previous example.

It is convenient to introduce the Helmholtz free energy function

$$\psi := \varepsilon - T\eta. \tag{34}$$

Then according to (28),(32)

$$\begin{aligned}
&\frac{\partial \psi}{\partial T} = \frac{\partial \varepsilon}{\partial T} - T\frac{\partial \eta}{\partial T} - \eta = -\eta \quad \Longrightarrow \quad \varepsilon = \psi + T\frac{\partial \psi}{\partial T}, \\
&\frac{\partial \varepsilon}{\partial \mathbf{g}} - T\frac{\partial \eta}{\partial \mathbf{g}} = 0 \quad \Longrightarrow \quad \psi = \psi\left(T\right) \quad \Longrightarrow \quad \varepsilon = \varepsilon\left(T\right).
\end{aligned} \tag{35}$$

Hence we have proven that the specific energy cannot depend on the temeperature gradient. This has been assumed in the simplified derivation of the heat conduction equation mentioned previously.

It remains to exploit the remaining part of the inequality (27) which contains a nonlinear dependence on the temperature gradient $\mathbf{g}$

$$\left[\Lambda\frac{\partial \mathbf{q}}{\partial T} - \frac{\partial \mathbf{h}}{\partial T}\right] \cdot \mathbf{g} \leq 0. \tag{36}$$

This is the so-called **residual inequality** which defines the **dissipation** in the system. If it is zero we have the state of thermodynamic equilibrium. Bearing the results (32), (33) in mind we can write this inequality in the following form

$$\frac{1}{T^2}Kg^2 \geq 0. \tag{37}$$

Hence the heat conductivity K cannot be negative. This means that the heat flux $\mathbf{q}$ is oriented from the hotter to the colder part of the body. This property is sometimes mistakenly identified with the second law of thermodynamics.

We have completed the exploitation of the second law of thermodynamics for our example. However we repeat these considerations in a different way to demonstrate the application of Lagrange multipliers in thermodynamics. This method has been designed in the PhD-Thesis of I-Shih Liu in 1973 (e.g. see [7, 2]). He has shown that instead of the direct elimination of some derivatives as we did above one can exploit an extended inequality in which all field equations are incorporated as constraints. In our simple example we have to replace the inequality (11) by the following one

$$\rho\frac{\partial \eta}{\partial t} + \operatorname{div}\mathbf{h} - \Lambda\left(\rho\frac{\partial \varepsilon}{\partial t} + \operatorname{div}\mathbf{q}\right) \geq 0, \tag{38}$$

where the Lagrange multiplier Λ, similarly to $\varepsilon, \mathbf{q}, \eta, \mathbf{h}$, can be a function of T and $\mathbf{g} = \operatorname{grad} T$. The existence of this multiplier and its dependence on the constitutive variables follows from Liu's theorem. If now the field T is chosen in such a way that it satisfies the field equation then the expression in the brackets vanishes and we have to satisfy the entropy inequality in the usual form. If it is not the case then the Lagrange multiplier must be chosen accordingly in order to correct the result for a non-zero value of the expression in the brackets. Hence this is indeed the same procedure as the one appearing in the classical mechanics with constraints.

The exploitation of the inequality (38) proceeds now in the same way as before. The chain rule of differentiation yields

$$\begin{aligned} &\frac{\partial T}{\partial t}\left[\rho\frac{\partial \eta}{\partial T} - \Lambda\rho\frac{\partial \varepsilon}{\partial T}\right] + \frac{\partial \mathbf{g}}{\partial t}\cdot\left[\rho\frac{\partial \eta}{\partial \mathbf{g}} - \Lambda\rho\frac{\partial \varepsilon}{\partial \mathbf{g}}\right] + \\ &+\mathbf{g}\cdot\left[\frac{\partial \mathbf{h}}{\partial T} - \Lambda\frac{\partial \mathbf{q}}{\partial T}\right] + \operatorname{grad}\mathbf{g}\cdot\left[\frac{\partial \mathbf{h}}{\partial \mathbf{g}} - \Lambda\frac{\partial \mathbf{q}}{\partial \mathbf{g}}\right] \geq 0. \end{aligned} \qquad (39)$$

This inequality must hold for arbitrary derivatives $\frac{\partial T}{\partial t}, \frac{\partial \mathbf{g}}{\partial t}$, $\operatorname{grad}\mathbf{g}$ and, simultaneously, it is linear with respect to these derivatives. Hence their coefficients must vanish and we obtain

$$\frac{\partial \eta}{\partial T} - \Lambda\frac{\partial \varepsilon}{\partial T} = 0, \quad \frac{\partial \eta}{\partial \mathbf{g}} - \Lambda\frac{\partial \varepsilon}{\partial \mathbf{g}} = 0, \quad \operatorname{sym}\left(\frac{\partial \mathbf{h}}{\partial \mathbf{g}} - \Lambda\frac{\partial \mathbf{q}}{\partial \mathbf{g}}\right) = 0, \qquad (40)$$

and there remains the residual inequality

$$\mathbf{g}\cdot\left[\frac{\partial \mathbf{h}}{\partial T} - \Lambda\frac{\partial \mathbf{q}}{\partial T}\right] \geq 0. \qquad (41)$$

These relations are identical with $(27)_2$, (28), (36). Hence together with the isotropy assumption we obtain exactly the same results as before.

Further in this work we use solely the method of multipliers. It seems to be simpler in the evaluation and it possesses certain additional properties convenient in the analysis of the so-called hyperbolic field equations which we will not discuss in this work.

4 Simple and Biot-type poroelastic nonlinear models

Macroscopic modeling of porous and granular materials belongs to the class of continuum theories. For many practical purposes it is sufficient to construct a single component model similar to this of elasticity or plasticity (e.g. hypoplasticity [8]), and, if necessary to extend such a model by a diffusion equation describing the relative motion of real components. Such procedures are commonly used in soil mechanics. However, dynamics and propagation of waves in porous materials as well as nonlinear effects such as large deformations, swelling, mass exchange processes, etc. require more sophisticated modeling. This follows usually the line proposed for mixtures of fluids by C. Truesdell in 1957 (see: [4, 9]) and extended by R. Bowen in 1982 ([10, 11]) to multicomponent porous materials. A linear multicomponent model of porous materials has been designed much earlier – in 1941– by Biot (see the collected papers of Biot on this subject [12]). This model and its various modifications are still successfully used in geophysical and biomechanical applications.

In this section we discuss some thermodynamic aspects of such a modeling. We begin with an introduction to a nonlinear continuum model in the so-called **Lagrangian description** and then present few important conclusions from the second law of thermodynamics for poroelastic materials. At the end of the section we present a linear version of poroelastic model which will be discussed in the next section of this work.

We consider a porous medium whose pores are filled with a mixture of A fluid components. The model is constructed on a chosen reference configuration $\mathcal{B}_0$ of the skeleton (the solid component), i.e. all fields are functions of a spatial variable $\mathbf{X} \in \mathcal{B}_0$, and time $t \in \mathcal{T}$. We consider a thermomechanical model in which the governing fields are as follows:

1. ρ^S – mass density of the skeleton in the reference configuration,
2. $\rho^\alpha, \alpha = 1, \dots, A$ – partial mass densities of fluid components refering to the unit volume of the reference configuration of the skeleton,
3. $\acute{\mathbf{x}}^S$ – velocity field of the skeleton,
4. $\mathbf{F}^S$ – deformation gradient of the skeleton,
5. $\acute{\mathbf{x}}^\alpha, \alpha = 1, \dots, A$ – velocity fields of fluid components,
6. T - absolute temperature of the skeleton,
7. n – porosity (the volume fraction of voids).

The mechanical part of these fields, i.e. fields 1. – 5., do not require any special justification. It should be solely stressed that the multiple velocity field $\left\{\acute{\mathbf{x}}^S, \acute{\mathbf{x}}^\alpha\right\}$ means that we include the diffusion in the system which is the main difference between this model and a model of composite materials. However, a single temperature requires already some explanation. In some physical systems such as ionized gases (plasma) different temperatures of components are quite natural. In plasma, for instance, electrons and ions possess different temperatures because they relax very slowly to a thermodynamic equilibrium with a common temperature. This is due to a big difference in mass of charged particles: ions – heavy and electrons – light. In soils different temperatures of components are primarily related to a different rate of heat transfer in a solid and in a fluid. Consequently, in many practical applications (for example in processes of freezing of water in soils) it would be justified to introduce more than only one temperature common for all components. This is not being done because a thermodynamics of such systems does not exist yet.

Another problem is connected with the choice of porosity as the only microstructural variable. First of all let us note that some properties of the microstructure are already appearing due to the fact that we are using a multicomponent model. One could work in such a model with a total mass density $\rho := \rho^S + \sum_{\alpha=1}^{A} \rho^\alpha$ and concentrations $c_\alpha := \dfrac{\rho^\alpha}{\rho}$. This would be the case for a mixture of fluids and concentrations would be microstructural variables of such a model. The presence of a solid requires an extension. For instance for empty pores all concentrations would be zero but still the microstructure would not be trivial. Hence the scalar field of porosity is a minimum extension which we have to make for porous materials. It does not seem to make sense to introduce any further volume fractions if there is solely one solid component. However, in many practical applications, for instance – for rocks, one may need two porosities (e.g. [13]) – one on the microscale (say – 10^{-2}m) and one on the macroscale of big macrocracks and clefts (say – 10m). There may be also the necessity to incorporate some additional parameters describing the geometry of channels such as tortuosity. We do not consider these generalizations in this work even though some of them can be treated by thermodynamic methods.

The above listed fields can be, of course, written in the Eulerian description characteristic for mixtures of fluids. We have then

$$\begin{aligned}
&\rho_t^S(\mathbf{x},t) := \rho^S\left(\mathbf{f}^{-1}(\mathbf{x},t),t\right) J^{S-1}\left(\mathbf{f}^{-1}(\mathbf{x},t),t\right), \quad J^S := \det \mathbf{F}^S, \\
&\rho_t^\alpha(\mathbf{x},t) := \rho^\alpha\left(\mathbf{f}^{-1}(\mathbf{x},t),t\right) J^{S-1}\left(\mathbf{f}^{-1}(\mathbf{x},t),t\right), \quad \alpha = 1,\ldots,A, \\
&\mathbf{v}^S(\mathbf{x},t) := \acute{\mathbf{x}}^S\left(\mathbf{f}^{-1}(\mathbf{x},t),t\right), \qquad (42)\\
&\mathbf{v}^\alpha(\mathbf{x},t) := \acute{\mathbf{x}}^\alpha\left(\mathbf{f}^{-1}(\mathbf{x},t),t\right), \quad \alpha = 1,\ldots,A, \\
&T(\mathbf{x},t) := T\left(\mathbf{f}^{-1}(\mathbf{x},t),t\right), \quad n(\mathbf{x},t) := n\left(\mathbf{f}^{-1}(\mathbf{x},t),t\right), \qquad (43)
\end{aligned}$$

where the function of motion of the skeleton

$$\mathbf{x} = \mathbf{f}(\mathbf{X},t), \tag{44}$$

is related to the velocity of the skeleton $\acute{\mathbf{x}}^S$ and to its deformation gradient $\mathbf{F}^S$ in the following way

$$\acute{\mathbf{x}}^S = \frac{\partial \mathbf{f}}{\partial t}, \quad \mathbf{F}^S = \operatorname{Grad} \mathbf{f}. \tag{45}$$

All fields listed above have purely macroscopic interpretation and, as usual in the continuum theory of mixtures, particles of all components are appearing simultaneously in each point of the domain. This means that processes which lead to a separation of components must be modelled on different domains separated by an interface. For instance the contact between a porous material saturated with water, and a porous material with empty pores requires the application of two models to two different domains and requires some contact conditions on the interface surrounding the saturated domain.

Macroscopic interpretation of fields yields frequently misunderstandings because some parts of the porous scientific community, particularly this stemming from the tradition of the pioneering work of Terzaghi, work with the so-called real (true) quantities, effective stresses, etc. Consequently in their interpretation the deformation of the skeleton is not describing changes of the macroscopic geometry of the system as it is the case in the present model but rather true deformations of grains on the microscopic level (real solid material), the partial mass densities are not refering to a common macroscopic volume of mixture but rather to partial volumes occupied by real components, etc. We return to this problem later in the work.

We proceed to define field equations for the above fields. Most of them follow as usual from partial balance equations.

In particular we have[4]

partial mass balance equations

$$\begin{aligned} \mathcal{E}^{\rho^S} &:= \frac{\partial \rho^S}{\partial t} - \hat{\rho}^S = 0, \\ \mathcal{E}^{\rho^\alpha} &:= \frac{\partial \rho^\alpha}{\partial t} + \mathrm{Div}\left(\rho^\alpha \acute{\mathbf{X}}^\alpha\right) - \hat{\rho}^\alpha = 0, \quad \alpha = 1, \dots, A, \\ \acute{\mathbf{X}}^\alpha &:= \mathbf{F}^{S-1}\left(\acute{\mathbf{x}}^\alpha - \acute{\mathbf{x}}^S\right), \end{aligned} \tag{46}$$

partial momentum balance equations

$$\begin{aligned} \mathcal{E}^{v^S} &:= \frac{\partial\left(\rho^S \acute{\mathbf{x}}^S\right)}{\partial t} - \left[\mathrm{Div}\,\mathbf{P}^S + \hat{\mathbf{p}}^S + \rho^S \mathbf{b}^S\right] = \mathbf{0}, \\ \mathcal{E}^{v^\alpha} &:= \frac{\partial\left(\rho^\alpha \acute{\mathbf{x}}^\alpha\right)}{\partial t} + \mathrm{Div}\left(\rho^\alpha \acute{\mathbf{x}}^\alpha \otimes \acute{\mathbf{X}}^\alpha\right) - \\ &\quad - \left[\mathrm{Div}\,\mathbf{P}^\alpha + \hat{\mathbf{p}}^\alpha + \rho^\alpha \mathbf{b}^\alpha\right] = \mathbf{0}, \quad \alpha = 1, \dots, A, \end{aligned} \tag{47}$$

partial energy balance equations

$$\begin{aligned} \mathcal{E}^{\varepsilon^S} &:= \frac{\partial}{\partial t}\left[\rho^S\left(\varepsilon^S + \frac{1}{2}\acute{x}^{S2}\right)\right] - \\ &\quad - \left[\mathrm{Div}\left(\mathbf{Q}^S - \mathbf{P}^{ST}\acute{\mathbf{x}}^S\right) + \rho^S \mathbf{b}^S \cdot \acute{\mathbf{x}}^S + \rho^S r^S + \hat{r}^S\right] = 0, \\ \mathcal{E}^{\varepsilon^\alpha} &:= \frac{\partial}{\partial t}\left[\rho^\alpha\left(\varepsilon^\alpha + \frac{1}{2}\acute{x}^{\alpha 2}\right)\right] + \mathrm{Div}\left[\rho^\alpha\left(\varepsilon^\alpha + \frac{1}{2}\acute{x}^{\alpha 2}\right)\acute{\mathbf{X}}^\alpha\right] - \\ &\quad - \left[\mathrm{Div}\left(\mathbf{Q}^\alpha - \mathbf{P}^{\alpha T}\acute{\mathbf{x}}^\alpha\right) + \rho^\alpha \mathbf{b}^\alpha \cdot \acute{\mathbf{x}}^\alpha + \rho^\alpha r^\alpha + \hat{r}^\alpha\right] = 0, \quad \alpha = 1, \dots, A, \end{aligned} \tag{48}$$

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[4] we define equations by various $\mathcal{E}$-symbols for typografical reasons – it simplifies the form of the entropy inequality appearing in further considerations.

balance equation of porosity

$$\mathcal{E}^n := \frac{\partial n}{\partial t} + \operatorname{Div}\mathbf{J} - \hat{n} = 0. \tag{49}$$

In these equations, all functions are defined on the reference configuration $\mathcal{B}_0$ of the skeleton. In this sense we may call it the **Lagrangian description** even though partial balance equations for fluid components contain convective parts with respect to the corresponding **Lagrangian velocities $\acute{\mathbf{X}}^\alpha$**.

The two-point tensors $\mathbf{P}^S, \mathbf{P}^\alpha$ denote the Piola-Kirchhoff partial stress tensors, $\mathbf{b}^S, \mathbf{b}^\alpha$ are partial body forces, $\varepsilon^S, \varepsilon^\alpha$ are partial densities of the internal energy, $\mathbf{Q}^S, \mathbf{Q}^\alpha$ – partial heat fluxes, r^S, r^α are partial energy radiations, $\mathbf{J}$ is the flux of porosity, and all quantities with a hat denote productions.

The balance equation of porosity (49) requires some explanation. We have argued in previous works on this subject (e.g. [14], [15]) that the balance equation for n follows from an averaging procedure for a representative elementary volume accounting for geometrical properties of the microstructure. However this argument is not needed if we make an extension of the continuous model of mixtures on the macroscopical phenomenological level. In such a case a new scalar field satisfies in the most general case a balance equation. Second order equations for microstructural variables appearing in some works on this subject (e.g. [16, 17]) indicate that most likely two variables rather than one additional microstructural variable should be introduced and one of them has to be eliminated from the model by substitution of one balance equation in another. The above balance equation for porosity specified for two-component poroelastic materials does not require additional boundary conditions – it possesses all properties of an evolution equation. Thermodynamic considerations indicate that the flux $\mathbf{J}$ results from the diffusion (relative motion of fluid components with respect to the skeleton), and the source $\hat{n}$ describes relaxation to the thermodynamic equilibrium.

Certainly we do not need all partial energy balance equations if we have to determine only one temperature field T. In such a case one relies on the bulk balance which follows from (48) by addition of equations for all components. Due to its relative complexity we will not present this equation in this work and refer the reader to the paper [18].

All bulk equations follow in the same way by adding partial equations. We make an assumption similar to this introduced by C. Truesdell for mixtures of fluids [9] that the bulk productions of mass, momentum, and energy vanish, i.e. the corresponding balance equations reduce to conservation laws. Hence

$$\hat{\rho}^S + \sum_{\alpha=1}^{A} \hat{\rho}^\alpha = 0, \quad \hat{\mathbf{p}}^S + \sum_{\alpha=1}^{A} \hat{\mathbf{p}}^\alpha = \mathbf{0}, \quad \hat{r}^S + \sum_{\alpha=1}^{A} \hat{r}^\alpha = 0. \tag{50}$$

Under these conditions we can introduce bulk quantities which correspond to those introduced by Truesdell for fluid mixtures which satisfy conservation laws of a single component continuum. Due to the fact that we have chosen one of the components – the skeleton – as a reference the form of these laws differs from the classical Lagrangian form of conservation equations of a single continuum.

As an example which we use later to transform the entropy inequaliy we present here two bulk quantities – the specific energy ε and the bulk heat flux vector $\mathbf{Q}$ – whose definitions follow by addition of partial energy equations $\mathcal{E}^{\varepsilon^S} + \mathcal{E}^{\varepsilon^\alpha}$. We quote here the results of the work [18]:

$$\begin{aligned} \rho\varepsilon := \quad & \sum_{\alpha=1}^{A} \rho^\alpha \varepsilon^\alpha + \rho^S \varepsilon^S + \\ & + \frac{1}{2}\left[\rho^S \mathbf{C}^S \cdot \left(\dot{\mathbf{X}} \otimes \dot{\mathbf{X}}\right) + \sum_{\alpha=1}^{A} \rho^\alpha \mathbf{C}^S \cdot \left(\acute{\mathbf{X}}^\alpha - \dot{\mathbf{X}}\right) \otimes \left(\acute{\mathbf{X}}^\alpha - \dot{\mathbf{X}}\right)\right], \end{aligned} \tag{51}$$

$$\begin{aligned} \mathbf{Q} := \quad & \sum_{\alpha=\mathbf{1}}^{\mathbf{A}} \mathbf{Q}^\alpha + \mathbf{Q}^S + \sum_{\alpha=1}^{A} \rho^\alpha \varepsilon^\alpha \left(\acute{\mathbf{X}}^\alpha - \dot{\mathbf{X}}\right) - \rho^S \varepsilon^S \dot{\mathbf{X}} - \\ & - \sum_{\alpha=1}^{A} \mathbf{P}^{\alpha T} \mathbf{F}^S \left(\acute{\mathbf{X}}^\alpha - \dot{\mathbf{X}}\right) + \mathbf{P}^{ST} \mathbf{F}^S \dot{\mathbf{X}} + \\ & + \frac{1}{2}\left[\sum_{\alpha=1}^{A} \rho^\alpha \left(\acute{\mathbf{X}}^\alpha - \dot{\mathbf{X}}\right) \otimes \left(\acute{\mathbf{X}}^\alpha - \dot{\mathbf{X}}\right) \otimes \left(\acute{\mathbf{X}}^\alpha - \dot{\mathbf{X}}\right) - \rho^S \dot{\mathbf{X}} \otimes \dot{\mathbf{X}} \otimes \dot{\mathbf{X}}\right] \mathbf{C}^S, \end{aligned} \tag{52}$$

where

$$\mathbf{C}^S := \mathbf{F}^{ST}\mathbf{F}^S, \quad \rho\dot{\mathbf{X}} := \sum_{\alpha=1}^{A} \rho^\alpha \acute{\mathbf{X}}^\alpha, \quad \rho := \rho^S + \sum_{\alpha=1}^{A} \rho^\alpha. \tag{53}$$

Obviously the bulk flux contains the contribution of partial heat fluxes. However it is related as well to the transport of energy due to the relative motion of components as well as the working of stresses on these relative motions. Hence in contrast to the single component continuum it is different from zero even in the case of isothermal processes in which partial heat fluxes vanish.

The formal thermodynamic construction of a continuous model proceeds as follows. We need field equations for the following set $\mathcal{F}$ of fields

$$\mathcal{F} := \left\{\rho^S, \rho^\alpha, \mathbf{F}^S, \acute{\mathbf{x}}^S, \acute{\mathbf{x}}^\alpha, T, n\right\}, \quad \alpha = 1, \ldots, A. \tag{54}$$

They follow from the balance equations for mass and momentum (46), (47), added energy balance equations (48), porosity balance (49), and relations (45) which indicate the following integrability condition

$$\mathcal{E}^F := \frac{\partial \mathbf{F}^S}{\partial t} - \operatorname{Grad} \acute{\mathbf{x}}^S = \mathbf{0}. \tag{55}$$

This plays the role of balance equation for the deformation gradient $\mathbf{F}^S$.

However, in order to transform these equations into field equations we have to perform the so-called **closure**. Namely the set $\mathcal{R}$ of the following quantities

$$\mathcal{R} := \left\{ \hat{\rho}^{\alpha}, \mathbf{P}^{S}, \mathbf{P}^{\alpha}, \hat{\mathbf{p}}^{\alpha}, \varepsilon, \mathbf{Q}, \mathbf{J}, \hat{n} \right\}, \quad \alpha = 1, \ldots, A, \tag{56}$$

must be specified in terms of fields and their derivatives in order to close the system. This is the **constitutive problem** defining materials contributing to the mixture. The mass and momentum sources for the skeleton do not appear in the above list because, according to (50), they are not independent. Let us remark that in many cases of practical bearing additional constitutive relations may have the form of evolution equations. For instance this is the case when the skeleton has some plastic properties. Then the effective stress must satisfy an evolution equation – the so-called Prandtl–Reuss equation for models of metals under small deformations or Kolymbas equation for hypoplastic models of soils [8]. When mass sources result from chemical reactions or adsorption/desorption processes their form is also given by an evolution equation, for instance by the Langmuir equation for adsorption processes.

We do not consider such problems in this work and limit further our attention to the so-called **poroelastic** materials. This assumption yields realistic models for biological tissues (e.g. lungs), woods, spongs, rocks etc. It is not very realistic for soils whose elastic properties are limited to some incremental processes. However even in this case such models are useful in description of waves of small amplitude, and, consequently, in a nondestructive testing of soils. Then the set of **constitutive variables** is as follows

$$\begin{aligned} \mathcal{C} \ &: = \left\{ \rho^{S}, \rho^{\alpha}, \mathbf{F}^{S}, \acute{\mathbf{X}}^{\alpha}, T, \mathbf{G}, n, \mathbf{N} \right\}, \\ \mathbf{G} \ &: = \operatorname{Grad} T, \quad \mathbf{N} := \operatorname{Grad} n, \quad \alpha = 1, \ldots, A, \end{aligned} \tag{57}$$

Usually this set is still much too complicated for the full thermodynamic analysis and one considers simpler models. For example in the case of a **simple two-component isotropic isothermal model without mass exchange** scalar constitutive functions depend on the following set of constitutive variables

$$\mathcal{C}_{simple} := \left\{ \rho^{F}, I, II, III, IV, V, VI, n \right\}, \tag{58}$$

where the six invariants $I, \ldots, VI$ are defined as follows

$$\begin{aligned} & I := \operatorname{tr} \mathbf{C}^{S}, \quad II := \frac{1}{2}\left(I^{2} - \operatorname{tr} \mathbf{C}^{S2} \right), \quad III := \det \mathbf{C}^{S}, \\ & IV := \acute{\mathbf{X}}^{F} \cdot \acute{\mathbf{X}}^{F}, \quad V := \acute{\mathbf{X}}^{F} \cdot \mathbf{C}^{S} \acute{\mathbf{X}}^{F}, \quad VI := \acute{\mathbf{X}}^{F} \cdot \mathbf{C}^{S2} \acute{\mathbf{X}}^{F}, \end{aligned} \tag{59}$$

with $\acute{\mathbf{X}}^{F}$ being the Lagrangian velocity of the single fluid component: $\alpha = F$. We present some results for such a model further in this paper.

The fundamental assumption of a continuous modeling has the form of the following constitutive relation

$$\mathcal{R} = \mathcal{R}\left(\mathcal{C}\right), \tag{60}$$

where the mapping $\mathcal{R}$ is assumed to be at least once continuously differentiable. The above relation is a short-cut notation for constitutive relations for each quantity of the set (56) which should be functions of variables (57).

The constitutive functions (60) are said to be **thermodynamically admissible** if any solution of field equations satisfies identically the following **entropy inequality**

$$\frac{\partial(\rho\eta)}{\partial t} + \operatorname{Div}\left(\rho\eta\dot{\mathbf{X}} + \mathbf{H}\right) \geq 0, \quad \eta = \eta(\mathcal{C}), \quad \mathbf{H} = \mathbf{H}(\mathcal{C}). \tag{61}$$

This is the Lagrangian form of the second law of thermodynamics proposed by I. Müller [7] for mixtures. The bulk entropy and the bulk entropy flux $\mathbf{H}$ are related to partial quantities in the following way

$$\rho\eta := \sum_{\alpha=1}^{A} \rho^\alpha \eta^\alpha + \rho^S \eta^S,$$

$$\mathbf{H} = \sum_{\boldsymbol{\alpha=1}}^{\mathbf{A}} \mathbf{H}^\alpha + \mathbf{H}^S + \sum_{\alpha=1}^{A} \rho^\alpha \eta^\alpha \left(\dot{\mathbf{X}}^{\alpha} - \dot{\mathbf{X}}\right) - \rho^S \eta^S \dot{\mathbf{X}}. \tag{62}$$

The flux $\mathbf{H}$ is **not** proportional to the bulk heat flux $\mathbf{Q}$ as it would be the case for many single component models. This is due to the fact that both fluxes contain explicit contributions of relative velocities. However we may still assume that the Fourier relations hold for partial fluxes

$$\mathbf{H}^S = \frac{\mathbf{Q}^S}{T}, \quad \mathbf{H}^\alpha = \frac{\mathbf{Q}^\alpha}{T}. \tag{63}$$

As we have already mentioned the exploitation of the condition (61) is based on the elimination of constraints imposed on the inequality by field equations. This can be done either by direct substitution or by means of auxiliary functions – Lagrange multipliers. We have demonstrated these pocedures on the example of the rigid heat conductor. In the present case we use the method of Lagrange multipliers besides the relation between the heat flux and the entropy flux which follows from the Fourier relations and the explicit relations for bulk fluxes. These will be substituted during the evaluation of the second law. Bearing the balance equations and constitutive relations in mind we write the entropy inequality in the following form

$$\begin{aligned} &\frac{\partial(\rho\eta)}{\partial t} + \operatorname{Div}\left(\rho\eta\dot{\mathbf{X}} + \mathbf{H}\right) - \Lambda^{\rho^S}\mathcal{E}^{\rho^S} - \sum_{\alpha=1}^{A} \Lambda^{\rho^\alpha}\mathcal{E}^{\rho^\alpha} - \\ &-\mathbf{\Lambda}^{v^S} \cdot \mathcal{E}^{v^S} - \sum_{\alpha=1}^{A} \mathbf{\Lambda}^{v^\alpha} \cdot \mathcal{E}^{v^\alpha} - \Lambda^\varepsilon \left(\mathcal{E}^{\varepsilon^S} + \sum_{\alpha=1}^{A} \mathcal{E}^{\varepsilon^\alpha}\right) - \mathbf{\Lambda}^n \mathcal{E}^n - \mathbf{\Lambda}^F \cdot \mathcal{E}^F \geq 0, \end{aligned} \tag{64}$$

where the Lagrange multipliers $\Lambda^{\rho^S}, \Lambda^{\rho^\alpha}, \mathbf{\Lambda}^{v^S}, \mathbf{\Lambda}^{v^\alpha}, \Lambda^\varepsilon, \Lambda^n, \mathbf{\Lambda}^F$ are functions of constitutive variables (57) (e.g. [2], [19]). The above inequality should hold not only for solutions of field equations but for **all** fields.

The evaluation of the above condition is tedious but straightforward. We have to apply the chain rule of differentiation and select linear contributions to the inequality. The requirement that this linear part is zero yields relations for multipliers and a set of thermodynamic identities restricting constitutive relations. There remains a residual, nonlinear inequality which defines the dissipation in the system. We quote here solely some results for a two–component system without presenting detailed derivations. These can be found in my earlier papers.

We proceed to present some results for isothermal processes in two-component systems: $\alpha = F$, where F denotes a single fluid component. It is convenient to introduce the specific partial Helmholtz free energies defined by the relations

$$\psi^S := \varepsilon^S - T\eta^S, \quad \psi^F := \varepsilon^F - T\eta^F. \tag{65}$$

Evaluation of the second law of thermodynamics has been made under the simplifying assumption that the constitutive dependence on two vectorial constitutive variables $\acute{\mathbf{X}}^F, \mathbf{N}$ is linear. This can be divided into two assumptions: partial Helmholtz free energies are independent of both variables, and in particular

$$\frac{\partial \psi^S}{\partial \acute{\mathbf{X}}^F} = \frac{\partial \psi^F}{\partial \acute{\mathbf{X}}^F} = 0, \tag{66}$$

and the constitutive dependence of the momentum source on the relative velocity $\acute{\mathbf{X}}^F$ as well as on the gradient of porosity $\mathbf{N}$ is linear, i.e.

$$\hat{\mathbf{p}} := \hat{\mathbf{p}}^S \equiv \hat{\mathbf{p}}^F = \pi \mathbf{F}^S \acute{\mathbf{X}}^F - \mathcal{N}\mathbf{N}. \tag{67}$$

Under these conditions thermodynamic identities imply the following relations.

- Partial stress tensors possess potentials - the partial Helmholtz free energies

  $$\mathbf{P}^S = \rho^S \frac{\partial \psi^S}{\partial \mathbf{F}^S}, \quad \mathbf{P}^F = -\left(\rho^{F2} \frac{\partial \psi^F}{\partial \rho^F} + n\mathcal{N}\right) \mathbf{F}^{S-T}, \tag{68}$$

  i.e. the stress tensor in the fluid component reduces to its spherical part – a partial pressure;

- Partial Helmholtz free energies depend on the following constitutive variables

  $$\psi^S = \psi^S\left(I, II, III, \rho^F\right), \quad \psi^F = \psi^F\left(III, \rho^F\right), \tag{69}$$

  and, in addition,

  $$2III \frac{\partial \psi^F}{\partial III} + \rho^F \frac{\partial \psi^F}{\partial \rho^F} = -\frac{\mathcal{N}}{\rho_0^{FR}}, \tag{70}$$

  where ρ_0^{FR} is a constant (the initial true mass density of the fluid).

As we see, both partial free energies are dependent on the third invariant of deformation of the skeleton, III, and on the partial mass density of the fluid, ρ^F. This means that the partial stress tensors contain a mechanical coupling between components – volume changes of one of them yield changes of stresses in the other component. In order to obtain this result the set of constitutive variables must include the gradient of porosity ($\mathcal{N} \neq 0$). Otherwise processes in components would be solely coupled through the source of momentum describing an influence of the diffusion. Let us mention that an analogous property has been discovered by I. Müller for mixtures of fluids (e.g. [7]). He has proven in 70'ies that mixtures of ideal fluids in which constitutive relations do not contain a dependence on gradients of partial mass densities (or, equivalently, concentrations) yield the discoupling of partial pressures. Such mixtures are called **simple**.

This type of coupling is characteristic for the so-called linear Biot model of porous materials. We present some of its features in the next section.

There remains the residual inequality in the form

$$\pi \left(\mathbf{F}^{ST}\acute{\mathbf{X}}^F\right) \cdot \left(\mathbf{F}^{ST}\acute{\mathbf{X}}^F\right) \geq 0. \tag{71}$$

Hence the only source of dissipation in these materials is the diffusion with the diffusion velocity $\mathbf{F}^{ST}\acute{\mathbf{X}}^F = \acute{\mathbf{x}}^F - \acute{\mathbf{x}}^S$.

We complete this section with **linearized** equations for two-component isotropic poroelastic materials in isothermal conditions. These equations serve the purpose to describe acoustic waves in porous materials which, in turn, form the basis for nondestructive testing of soils and rocks. In such a case the Lagrangian description is identical with the Eulerian description and we can use fields transformed according to relations (42). The assumption on linearity means that we consider processes satisfying the following restrictions

$$\max\left\{\left|\lambda^{(\alpha)}\right|\right\}_{\alpha=1,2,3} \ll 1, \quad |\epsilon| \ll 1, \quad \epsilon := -\frac{\rho_t^F - \rho_0^F}{\rho_0^F}, \tag{72}$$

where $\lambda^{(\alpha)}$ are eigenvalues of the Almansi-Hamel deformation tensor of the skeleton

$$\det\left(\mathbf{e}^S - \lambda\mathbf{1}\right) = 0, \quad \mathbf{e}^S := \frac{1}{2}\left(\mathbf{1} - \mathbf{F}^{ST^{-1}}\mathbf{F}^{S^{-1}}\right), \tag{73}$$

and ρ_0^F, ϵ denote a constant initial partial mass density of the fluid, and small macroscopic volume changes of the fluid, respectively.

Under these assumptions the constitutive relations for partial Cauchy stresses follow from the general relations (68) in the following form

$$\begin{aligned}
\mathbf{T}^S &= \mathbf{T}_0^S + \lambda^S e\mathbf{1} + 2\mu^S\mathbf{e}^S + \beta\left(n - n_E\right)\mathbf{1} + n_0\mathcal{N}\epsilon\mathbf{1}, \\
\mathbf{T}^S &:= \left(III\right)^{-\frac{1}{2}}\mathbf{P}^S\mathbf{F}^{ST}, \quad e := \operatorname{tr}\mathbf{e}^S, \\
\\
\mathbf{T}^F &= -p_0^F\mathbf{1} + \left(\rho_0^F\kappa\epsilon + n_0\mathcal{N}e\right)\mathbf{1} + \beta\left(n - n_E\right)\mathbf{1}, \\
\mathbf{T}^F &:= \left(III\right)^{-\frac{1}{2}}\mathbf{P}^F\mathbf{F}^{ST},
\end{aligned} \tag{74}$$

where the material parameters $\lambda^S, \mu^S, \kappa, \beta, \mathcal{N}$ depend solely on the initial constant porosity n_0. $\mathbf{T}_0^S, p_0^F$ are an initial partial stress in the skeleton, and an initial partial pressure in the fluid, respectively. The equilibrium value of the porosity n_E is given by the relation

$$n_E = n_0 \left(1 + e - \epsilon\right), \tag{75}$$

which follows from the evaluation of the porosity equation in the thermodynamic equilibrium: $\mathbf{v}^F = \mathbf{v}^S, \hat{n} = 0$. It is clear that changes of porosity described by the difference $n_E - n_0$ correspond to undrained conditions and there is no spontaneous relaxation of porosity in the thermodynamic equilibrium.

The momentum balance equations have in this case the following form

$$\begin{aligned} \rho_0^S \frac{\partial \mathbf{v}^S}{\partial t} &= \operatorname{div} \mathbf{T}^S + \pi \left(\mathbf{v}^F - \mathbf{v}^S\right) - \mathcal{N} \operatorname{grad} n_E + \rho_0^S \mathbf{b}^S, \\ \rho_0^F \frac{\partial \mathbf{v}^F}{\partial t} &= \operatorname{div} \mathbf{T}^F - \pi \left(\mathbf{v}^F - \mathbf{v}^S\right) + \mathcal{N} \operatorname{grad} n_E + \rho_0^F \mathbf{b}^F, \end{aligned} \tag{76}$$

where ρ_0^S is the initial partial mass density of the skeleton, and $\rho_0^S \mathbf{b}^S, \rho_0^F \mathbf{b}^F$ are partial external body forces.

Simultaneously an influence of the difference $n - n_E$ on in the analysis of acoustic waves can be approximately neglected due to the smallness of parameter β. Substitution of relations (74) and (75) in the above set yields

$$\begin{aligned} \rho_0^S \frac{\partial \mathbf{v}^S}{\partial t} &= \operatorname{div} \left(\mathbf{T}_0^S + K e \mathbf{1} + 2\mu^S \operatorname{dev} \mathbf{e}^S + Q \epsilon \mathbf{1}\right) + \pi \left(\mathbf{v}^F - \mathbf{v}^S\right) + \rho_0^S \mathbf{b}^S, \\ \rho_0^F \frac{\partial \mathbf{v}^F}{\partial t} &= -\operatorname{grad} \left(p_0^F + R\epsilon + Qe\right) \operatorname{div} \mathbf{T}^F - \pi \left(\mathbf{v}^F - \mathbf{v}^S\right) + \rho_0^F \mathbf{b}^F, \end{aligned} \tag{77}$$

where

$$K := \lambda^S + \frac{2}{3}\mu^S - n_0 \mathcal{N}, \quad Q := 2 n_0 \mathcal{N}, \quad R := \rho_0^F \kappa - n_0 \mathcal{N}, \tag{78}$$

$$\operatorname{dev} \mathbf{e}^S := \mathbf{e}^S - \frac{1}{3} \operatorname{tr} \mathbf{e}^S \mathbf{1}.$$

In the next section we discuss some aspects of the identification of the material parameters appearing in this set of equations.

5 Micro-macro-transitions for linear poroelastic materials

One of the main problems in applications of the linear poroelastic model is the dependence of material parameters K, μ^S, R, Q on the porosity n_0. In order to find this dependence one has to relate macroscopic and microscopic descriptions of processes. We should stress that the meaning of the microscopic description for geotechnical materials is different from this used, for instance, in materials science.

The characteristic length of geotechnical microstructure is almost macroscopic (say – 1mm) and, therefore, we can describe microstructural processes by continuum theories as we do in the case of macroscopic description. The difference is solely related to very complicated domains in the microscopic description which make impossible a solution of real boundary value problems and require a construction of some averages.

In the case of the shear modulus μ^S for granular materials the problem cannot be solved on the basis of linear considerations. Properties of this modulus depend on interactions between grains and these in turn must be at least dependent on the pressure confining the system. Consequently this macroscopic parameter cannot be constant – it must be dependent on one of the macroscopic fields. Hence the model cannot be linear. There are some attempts to solve this problem by means of a kinetic theory of granular materials (e.g. [20]) but these are still rather far from engineering applications.

The situation is different in the case of the compressibility moduli. Some relations have been proposed already at the beginning of 20th century (e.g. [21]) and the results obtained by Gassmann 1951 [22] are used until today. We present here only the main features of this approach in order to point out the role of rational thermodynamics in this problem.

We consider a chosen point of the two-component continuum and assume that macroscopic constitutive properties of this medium are described by volume averages calculated over the so-called Representative Elementary Volume (REV) of the microstructure. This means that a real material behaviour is replaced by a certain amount of smoothed out data. In the case of mechanical properties related to the compressibility we assume that states of the system in REV are **homogeneous** and all processes are **quasistatic**. In addition we define the elementary representative volume as **material** with respect to the solid component.

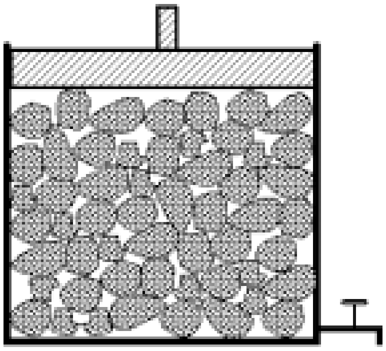

Figure 2: *Scheme of the jacketed test*

On the macroscopic level the constitutive relations are given by (74). In the case of purely volumetric changes we can write them in the following form

$$p^S = p_0^S - Ke + Q\frac{\rho_t^F - \rho_0^F}{\rho_0^F}, \quad p^F = p_0^F + R\frac{\rho_t^F - \rho_0^F}{\rho_0^F} - Qe, \tag{79}$$

$$p^S := -\frac{1}{3}\mathrm{tr}\,\mathbf{T}^S, \quad p^F := -\frac{1}{3}\mathrm{tr}\,\mathbf{T}^F,$$

where the notation (78) has been used. In these relations p_0^S, p_0^F denote the reference partial pressures in the skeleton and in the fluid, respectively. We are using here again the mass densities of the fluid component ρ_t^F, ρ_0^F rather than volume changes ϵ because the partial mass density or the partial specific volume (compare section 3) are proper local constitutive variables for the fluid, and the volume change ϵ may be not for homogeneous processes. This appears, for instance, in simple tests considered in this section when the total mass of the fluid is not preserved (drainage!). In the local description this problem would not appear because the local mass conservation does hold. However it requires a local velocity of fluid to be different from zero which cannot be properly incorporated in global homogeneous models. The problem does not appear for the skeleton because the mass of skeleton is conserved also in homogeneous tests.

Let M^S denote the instantaneous mass of the solid component in REV, and M^F – the instantaneous mass of the fluid in REV. We assume that the constitutive relations on the microscopic level are of the form

$$p^{SR} = p_0^{SR} - K_s \frac{\rho_0^{SR} - \rho_t^{SR}}{\rho_0^{SR}}, \quad p^{FR} = p_0^{FR} - K_f \frac{\rho_0^{FR} - \rho_t^{FR}}{\rho_0^{FR}}, \tag{80}$$

where $\rho_t^{SR} = \frac{M^S}{V^S}$ is the true mass density of the skeleton (comp. section 3), $\rho_t^{FR} = \frac{M^F}{V^F}$ denotes the true mass density of the fluid, K_s is the so-called bulk modulus of the solid material composing the porous frame (compressibility modulus of grains), and K_f is the bulk (real) modulus of the fluid. The index zero refers to the initial state.

We want to find the relation between the macroscopic parameters K, R, Q, the microscopic parameters K_s, K_f, and the porosity n_0. To this aim Biot and Willis [5] designed two simple tests: the unjacketed test whose some elements we have already discussed earlier in this work, and the jacketed drained test shown schematically in Fig.2 (open tap). The third possibility appears for the jacketed undrained test (closed tap).

In all possible tests of this sort we have to satisfy the following relations

1. macro- and micro- constitutive relations given by (79), (80), respectively,
2. geometrical compatibility relations which follow from the assumption that REV is material with respect to the solid component,
3. dynamical compatibility relations between micro- and macro-pressures

$$p^S = (1 - n_0)\, p^{SR}, \quad p^F = n_0 p^{FR}, \tag{81}$$

which result from the assumption on randomness of microstructure (i.e. that the volume fraction of voids – porosity n_0 is identical with the fraction of the area of surface of voids to the total area in an arbitrary cross-section of REV),

4. equilibrium condition with an external excess pressure p' loading the system

$$p' = \left(p^S - p_0^S\right) + \left(p^F - p_0^F\right), \tag{82}$$

5. relations defining the tests.

We proceed to derive the geometrical compatibility relations. If we denote the volume of REV by V then in any homogeneous quasistatic process the mass $M^S = \rho_t^S V$ must be conserved

$$\frac{d\rho_t^S V}{dt} = 0 \quad \Longrightarrow \quad \frac{\rho_t^S}{\rho_0^S} = \frac{V_0}{V} = \frac{1}{1+e}, \tag{83}$$

where V_0 is the initial volume of REV. The formula means that we assume for the whole volume of REV the macroscopic rule of volume changes.

Simultaneously on the microscopic level we have $\rho_t^{SR} = \dfrac{M^S}{V^S}$ and due to the definition of porosity (volume fraction of voids) $1 - n = \dfrac{V^S}{V}$ we obtain

$$\rho_t^S = (1-n)\,\rho_t^{SR} \quad \Longrightarrow \quad \frac{1-n}{1-n_0}\frac{\rho_t^{SR}}{\rho_0^{SR}} = \frac{1}{1+e}. \tag{84}$$

On the other hand the mass conservation can be written in its microscopic form

$$\frac{d\rho_t^{SR} V^S}{dt} = 0 \quad \frac{\rho_t^{SR}}{\rho_0^{SR}} = \frac{V_0^S}{V^S} = \frac{1}{1+e^R}. \tag{85}$$

The combination of the results (84) and (85) yields the first geometrical compatibility relation

$$\frac{1-n}{1-n_0} = \frac{1+e^R}{1+e}. \tag{86}$$

This relation shows the difference between the notion of volume changes in the macroscopic model of porous materials and real volume changes of grains. Even if the material of grains is assumed to be approximately incompressible ($e^R \equiv 0$) the macroscopic changes of volume of the skeleton e are different from zero due to changes of porosity.

The second relation follows from the transformation of fluid volume (voids)

$$V^F = V_0^F\left(1 + \epsilon^R\right) \quad \Longrightarrow \quad \frac{n}{n_0} = \frac{1+\epsilon^R}{1+e}. \tag{87}$$

This is the second geometrical compatibility relation.

Easy manipulations on those two compatibility relations yield the following relation between the macroscopic change of the volume and microscopic changes of volumes of both components.

$$e = (1 - n_0)\, e^R + n_0 \epsilon^R. \tag{88}$$

It remains to define the tests. It is easy to see that the following conditions must hold:

1. Undrained jacketed test: the mass of fluid is conserved, i.e.

   $$\frac{d\rho_t^F V}{dt} = 0 \quad \Longrightarrow \quad \rho_t^F = \frac{\rho_0^F}{1+e} \quad \Longrightarrow \quad \frac{n}{n_0}\frac{\rho_t^{FR}}{\rho_0^{FR}} = \frac{1}{1+e},$$

   and

   $$\frac{d\rho_t^{FR} V^F}{dt} = 0 \quad \Longrightarrow \quad \frac{\rho_t^{FR}}{\rho_0^{FR}} = \frac{1}{1+\epsilon^R}.$$

   Combination of these two relations shows that we obtain again the relation (87). This means that this test does not give any additional information about micro-macrorelations.

2. Drained jacketed test: in this case the increment of the pore pressure in the fluid must be zero if the continuity of the pressure is preserved in the tap

   $$p^{FR} - p_0^{FR} = 0. \tag{89}$$

   This seems to be a safe assumption for quasistatic processes because, in contrast to the unjacketed test discussed at the beginning of this work, there are no surface effects possible.This test is usually used in practice to define the so-called drained compressibility modulus of the skeleton K_d.

3. Unjacketed test: as we have shown in section 3 we can assume in this case that the pore pressure is in equilibrium with the excess external pressure

   $$p^{FR} - p_0^{FR} = p'. \tag{90}$$

The above relations can be combined to give the desired relation between microscopic and macroscopic compressibilities.

This is not what is done in the literature on the subject. In those considerations the undrained jacketed test is fully ignored, the drained jacketed test is used, as already mentioned, to define the drained compressibility modulus K_d and the unjacketed test is considered under the assumption that the porosity remains constant (e.g. [6]). Then we obtain after easy calculations (e.g. see [23, 24])

$$\begin{aligned} K &= K_d + \frac{\alpha^2}{\dfrac{\alpha - n_0}{K_s} + \dfrac{n_0}{K_f}}, \quad R = \frac{n_0}{\dfrac{\alpha - n_0}{K_s} + \dfrac{n_0}{K_f}}, \\ Q &= \frac{n_0 \alpha}{\dfrac{\alpha - n_0}{K_s} + \dfrac{n_0}{K_f}}, \quad \alpha := 1 - \frac{K_d}{K_s}. \end{aligned} \tag{91}$$

These are the so-called Gassmann relations. α is called the Biot-Willis parameter.

It seems to be a wonder that with all these assumptions the above relations give good results in practical applications, for instance – in the wave analysis. It is clear that the validity of the above relations is limited in many ways. The assumption on the constant porosity seems to be at least doubtful, the validity of the relation between pressures on the interface in the unjacketed experiment is limited to very simple systems, as discussed in Sect.3. If any of the effects listed in this section should be incorporated then we have to rely on the continuity of the free enthalpy rather than on the continuity of pressure. This should be, for instance, the case for viscous fluids even though the problem is ignored in the literature (compare the analysis of acoustic waves in porous materials in [6]).

Practical application in nondestructive testing follows now from measurements of speeds of propagation of bulk or surface waves in soils or rocks. These experimental data predict macroscopic elastic parameters combined with mass densities. Combination of those data with Gassmann relations (91) yields the relation for porosity. This procedure has been investigated in a recent paper of Foti, Lai and Lancellotta [25]. Results compare well with experimental findings.

6 Concluding remarks

Results presented in this article are typical for macroscopic thermodynamic modeling of continuous media. Consequently we can state that the results of evaluation of the second law of thermodynamics possess two features

- they reduce the extent of requirements concerning the construction of constitutive laws and frequently – this is the case for a rather broad class of poroelastic materials discussed in section 3 – they yield the existence of thermodynamic potentials. The latter not only simplify the construction of constitutive laws but enable an analysis of existence and stability of solutions which we did not discuss in this work;
- they clarify limitations of ad hoc models appearing in practical applications. The example of the Gassmann relations discussed in the paper shows that an extention of these relations on, for instance, viscous fluids may not be as straightforward as sometimes done in works on the subject.

Simultaneously the thermodynamic method and, in particular, the second law of thermodynamics do not give specific results which could replace experiments. In some cases of material properties such as the heat conductivity or permeability of porous media we obtain solely inequalities restricting the models but not even hints how to evaluate the material parameters without solving field equations and verifying solutions by experiments.

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