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Mass exchange, diffusion and large deformations of poroelastic materials

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Dedicated to Professor Kolumban Hutter of the University of Darmstadt on occasion of his 60th birthday.

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Contents

Summary

The paper contains a review of fundamental equations of the two component thermoporoelastic materials with the balance equation of porosity. By means of the exploitation of the second law of thermodynamics restricted to small deviations from thermodynamical equilibrium it is proven that there exists no thermodiffusional coupling of components through intrinsic parts of fluxes. Certainly such a coupling is still present due to convective contributions. Simultaneously we show that classical partial dynamical compatibility conditions on material interfaces cannot hold. For boundary conditions on permeable boundaries to hold true it must be required that global balance equations contain at least surface sources of momentum, entropy, and porosity. We show as well that the requirement of the local thermodynamical equilibrium on permeable interfaces yields the continuity of absolute temperature. It means that temperature becomes a measurable physical field in porous materials undergoing processes with small deviations from thermodynamical equilibria. This result allows to extend models of mass exchange in poroelastic materials from adsorption isothermal processes to chemical reactions, and phase transformations. Details of the latter problems are not discussed in this paper.

1 Introduction

The paper is devoted to the presentation of basic properties of the thermodynamical model of thermoporoelstic materials which I have developed during the last decade. A good deal of material contained in this work has been already published elsewhere, and I quote it here again to make the paper selfcontained, and new contributions understandable. The presentation of one chosen model of porous materials does not mean, of course, that there exists any qualification for various models appearing in the literature. An appropriate one must be always chosen fitting best the purpose. For instance, the model presented in this paper is particularily well suited to describe wave propagation in multicomponent systems, as well as large deformations of the skeleton. It is much too complex in applications to most consolidation problems. A model in which one assumes the incompressibility of components frequently used in soil mechanics cannot describe all modes of acoustic and surface waves but it describes very well various instabilities in granular geotechnical materials such as piping. A model based on Darcy law with rigid skeleton descirbes very well flows of fluid components (reaction-diffusion equations) but it cannot describe consolidation processes, and acoustic waves. One can multiply such examples.

Due to the above limitation of the contents the references are chose in a very subjective manner, and reflect solely results for one particular approach.

The general part of the present considerations is devoted to a two component system consisting of an elastic skeleton (a solid component), and of the ideal fluid. Deformations, and kinematics of both components are related to a reference configuration of the skeleton. This is called the Lagrangian description of motion [1]. The main new elements of the model presented in this work are contained in the exploitation of the second law of thermodynamics which yields quite explicit relations for fluxes of the balance equations under the assumption of small deviations from the thermodynamical equilibrium state. We do not make an assumption on a relation between partial heat, and entropy fluxes which has been made in the thermodynamical analysis of a multicomponent system in [2, 3]. In addition we present an analysis of conditions on interfaces material with respect to the skeleton. This analysis allows to interpret the temperature in the classical way for processes satisfying the above assumption on small deviations. This means that we can effectively construct boundary conditions for heat conduction problems.

In Section 4 we review briefly results on adsorption processes coupled to the diffusion. This problem indicates limitations of the contemporary modeling of mass exchange in porous materials which is related to the assumption that processes are isothermal. Results on nonisothermal models presented in this work allow to extend the description to processes in which we have to incorporate the latent heats of phase transformations, and heats of chemical reactions.

The paper is organized in the following way. Sections 2 and 3 contain the development of the general thermodynamical two component model. Technical considerations connected with the exploitation of the second law of thermodynamics are shifted to the Appendix. Section 4 is devoted to modeling of adsorption. Section 5 contains an analysis of the structure of conditions on interfaces material with respect to the skeleton. In particular we present sufficient conditions for the continuity of absolute temperature on such an interface.

2 Balance equations in Lagrangian description

Large deformations of the skelton of porous materials yield the necessity of Lagrangian description of motion. This has been proposed in a series of works [1, 4, 2] and some details can be found in the book [5]. In this Section I present only some main features of this description.

We consider a two-component porous medium described as a continuum. The motion of the skeleton is assumed to be given by a diffeomorphism

$$\mathbf{f}^S(\cdot,\cdot) : B \times T \to \mathbb{R}^3, \tag{2.1}$$

where B is a reference configuration of the skeleton, $B \subset \mathbb{R}^3$, and T is the time interval. The deformation gradient, and the partial velocity of the skeleton are defined by the relations

$$\mathbf{F}^S = \operatorname{Grad} \mathbf{f}^S, \qquad \acute{\mathbf{x}}^S = \frac{\partial \mathbf{f}^S}{\partial t}, \tag{2.2}$$

and they are assumed to be continuous almost everywhere in B. The motion of the fluid component is assumed to be given by a partial velocity field

$$\acute{\mathbf{x}}^F : B \times T \to \mathbb{V}^3, \tag{2.3}$$

where $\mathbb{V}^3$ is the three dimensional vector space. The partial fluid velocity is assumed to be continuous almost everywhere in B. Material domains of the skeleton $\mathcal{P} \subset B$ are assumed to satisfy usual conditions of continuum mechanics which we shall not quote here. Certainly they also do not depend on time, and each member of their class $\mathbb{M}^S$ is called S-material. On the other hand, material domains of the fluid $\mathcal{P} \subset B$ do depend on time, and their kinematics is described by the Lagrangian velocity field $\acute{\mathbf{X}}^F$:

$$\acute{\mathbf{X}}^F := \mathbf{F}^{S-1}(\acute{\mathbf{x}}^F - \acute{\mathbf{x}}^S). \tag{2.4}$$

The members of their class $\mathbb{M}^F$ are called F-material.

The set of fields characterizing temperature dependent processes of motion in porous media is of the form

$$\left\{\rho^S, \rho^F, \mathbf{f}^S, \acute{\mathbf{x}}^F, n, \Theta\right\}, \tag{2.5}$$

where ρ^S, ρ^F are partial mass densities in the reference configuration B, n is the porosity, and Θ is the absolute temperature. We return later very briefly to the problem of systems with multiple temperatures.

In the case of porous media, whose heterogeneity is limited to an interface Σ dividing the refernce configuration into two subdomains, B^+, B^-, $c\ell B^+ \cup c\ell B^- = c\ell B$, $c\ell B^+ \cap c\ell B^- = \Sigma$, where $c\ell$ denotes the closure of domains in which the porous medium may have different material properties, we have the following set of balance equations corresponding to fields (2.5)

- partial mass balance

$$\forall \mathcal{P} - S - \text{material}: \qquad \frac{d}{dt}\int_{\mathcal{P}} \rho^S dv = \int_{\mathcal{P}} \hat{\rho}^S dV, \tag{2.6}$$

$$\forall \mathcal{P} - F - \text{material}: \qquad \frac{d}{dt}\int_{\mathcal{P}} \rho^F dv = \int_{\mathcal{P}} \hat{\rho}^F dV, \qquad \hat{\rho}^S + \hat{\rho}^F = 0 \tag{2.7}$$

- partial momentum balance

$\forall \mathcal{P} - S - \text{material}:$

$$\frac{d}{dt}\int\limits_{\mathcal{P}} \rho^S \acute{\mathbf{x}}^S dV = \oint\limits_{\partial\mathcal{P}} \mathbf{P}^S \mathbf{N} dA + \int\limits_{\mathcal{P}} \hat{\mathbf{p}}^S dV + \oint\limits_{\mathcal{P}\cap\Sigma} \hat{\mathbf{p}}^S_{surf} dA, \tag{2.8}$$

$\forall \mathcal{P} - F - \text{material}:$

$$\frac{d}{dt}\int\limits_{\mathcal{P}} \rho^F \acute{\mathbf{x}}^F dV = \oint\limits_{\partial\mathcal{P}} \mathbf{P}^F \mathbf{N} dA + \int\limits_{\mathcal{P}} \hat{\mathbf{p}}^F dV + \oint\limits_{\mathcal{P}\cap\Sigma} \hat{\mathbf{p}}^F_{surf} dA,$$

$$\hat{\mathbf{p}}^S + \hat{\mathbf{p}}^F = 0, \qquad \hat{\mathbf{p}}^S_{surf} + \hat{\mathbf{p}}^F_{surf} = 0, \tag{2.9}$$

- partial energy balance

$\forall \mathcal{P} - S - \text{material}:$

$$\frac{d}{dt}\int\limits_{\mathcal{P}} \rho^S \left(\varepsilon^S + \tfrac{1}{2}\acute{x}^{S2}\right) dV + \oint\limits_{\partial\mathcal{P}} \mathbf{Q}^S \cdot \mathbf{N} dA = \oint\limits_{\partial\mathcal{P}} \left(\mathbf{P}^S \mathbf{N}\right) \cdot \acute{\mathbf{x}}^S dA, \tag{2.10}$$

$\forall \mathcal{P} - F - \text{material}:$

$$\frac{d}{dt}\int\limits_{\mathcal{P}} \rho^F \left(\varepsilon^F + \tfrac{1}{2}\acute{x}^{F2}\right) dV + \oint\limits_{\partial\mathcal{P}} \mathbf{Q}^F \cdot \mathbf{N} dA = \oint\limits_{\partial\mathcal{P}} \left(\mathbf{P}^F \mathbf{N}\right) \cdot \acute{\mathbf{x}}^F dA,$$

- balance of porosity

$\forall \mathcal{P} - S - \text{material}:$

$$\frac{d}{dt}\int\limits_{\mathcal{P}} n dV + \oint\limits_{\partial\mathcal{P}} \mathbf{J} \cdot \mathbf{N} dA = \int\limits_{\mathcal{P}} \hat{n} dV + \int\limits_{\mathcal{P}\cap\Sigma} \hat{n}_{surf} dA. \tag{2.11}$$

The sources of mass $\hat{\rho}^S, \hat{\rho}^F$, the volume sources of momentum $\hat{\mathbf{p}}^S, \hat{\mathbf{p}}^F$, and the surface sources of momentum $\hat{\mathbf{p}}^S_{surf}, \hat{\mathbf{p}}^F_{surf}$ are assumed to satisfy the local conservation laws (2.7), (2.9). This condition can be weakened which is not essential for considerations of this work. We justify the necessity of the presence of momentum surface sources and porosity surface source on the interface in Section 5.

The partial Piola-Kirchhoff stress tensors are denoted by $\mathbf{P}^S, \mathbf{P}^F$, the heat flux vectors are $\mathbf{Q}^S, \mathbf{Q}^F$. $\hat{n}, \hat{n}_{surf}$ denote the volume source, and the surface source of porosity, respectively. The flux of porosity is denoted by $\mathbf{J}$. $\mathbf{N}$ is a unit vector orthogonal to the surface ∂P.

The local form of these equations in $B \backslash \Sigma$ is as follows

$$
\begin{aligned}
& \frac{\partial \rho^S}{\partial t} = \hat{\rho}^S, \qquad \frac{\partial \rho^F}{\partial t} + \operatorname{Div}(\rho^F \acute{\mathbf{X}}^F) = \hat{\rho}^F, \\
& \frac{\partial \rho^S \acute{\mathbf{x}}^S}{\partial t} = \operatorname{Div} \mathbf{P}^S + \hat{\mathbf{p}}^S, \quad \frac{\partial \rho^F \acute{\mathbf{x}}^F}{\partial t} + \operatorname{Div}\left(\rho^F \acute{\mathbf{x}}^F \otimes \acute{\mathbf{X}}^F - \mathbf{P}^F\right) = \hat{\mathbf{p}}^F, \\
& \frac{\partial \rho^S (\varepsilon^S + \frac{1}{2} \acute{x}^{S2})}{\partial t} + \operatorname{Div}\left(\mathbf{Q}^S - \mathbf{P}^{ST} \acute{\mathbf{x}}^S\right) = 0, \\
& \frac{\partial \rho^F (\varepsilon^F + \frac{1}{2} \acute{x}^{F2})}{\partial t} + \operatorname{Div}\left(\rho^F \left(\varepsilon^F + \tfrac{1}{2} \acute{x}^{F2}\right) \acute{\mathbf{X}}^F + \mathbf{Q}^F - \mathbf{P}^{FT} \acute{\mathbf{x}}^F\right) = 0, \\
& \frac{\partial n}{\partial t} + \operatorname{Div} \mathbf{J} = \hat{n},
\end{aligned}
\tag{2.12}
$$

where $\acute{\mathbf{X}}^F$ denotes the Lagrangian relative velocity (see (2.4)). We use these equations to construct field equations for thermoporoelastic materials.

3 Thermodynamics of thermoporoelastic materials

In order to close the system (2.12) and obtain field equations, and boundary conditions for fields (2.5) we need constitutive relations for the following constitutive quantities

$$
\mathcal{Z} := \left\{ \hat{\rho}^S, \hat{\rho}^F, \mathbf{P}^S, \mathbf{P}^F, \hat{\mathbf{p}}^S, \hat{\mathbf{p}}^S_{surf}, \hat{\mathbf{p}}^F, \hat{\mathbf{p}}^F_{surf}, \varepsilon^S, \varepsilon^F, \mathbf{Q}^S, \mathbf{Q}^F, \mathbf{J}, \hat{n}, \hat{n}_{surf} \right\}. \tag{3.1}
$$

Certainly, constitutive relations for sources are not all independent due to conservation laws.

We assume the quantities $\mathcal{Z}$ to be differentiable functions of the following constitutive variables

$$
\mathcal{C} := \left\{ \rho^S, \rho^F, \mathbf{F}^S, \acute{\mathbf{X}}^F, n, \Theta, \mathbf{G} \right\}, \qquad \mathbf{G} := \operatorname{Grad} \Theta, \tag{3.2}
$$

i.e.

$$\mathcal{Z} = \mathcal{Z}(\mathcal{C}). \tag{3.3}$$

As we see further we need additional fields of microstructural variables in order to describe processes of mass exchange. We introduce them in the next Section as they do not influence basic consequences of the second law of thermodynamics which we proceed to present.

Any solution of field equations which follows from (2.12) by the substitution of (3.3) we call the thermodynamical process. As we consider solely the case of the common temperature for the solid and the fluid we use the energy balance in the bulk form which follows by adding equations $(2.12)_5$ and $(2.12)_6$.

The second law is assumed to be constructed in the same way as the balance equations of Section 2. We assume an existence of nontrivial fields of partial entropies η^S, η^F, and their fluxes $\mathbf{H}^S, \mathbf{H}^F$ such that

$$\forall\mathcal{P} - S - \text{material}: \qquad \frac{d}{dt}\int\limits_{\mathcal{P}} \rho^S \eta^S dV + \int\limits_{\mathcal{P}} \operatorname{Div}\mathbf{H}^S dV = \int\limits_{\mathcal{P}} \hat{\eta}^S dV + \int\limits_{\mathcal{P}\cap\Sigma} \hat{\eta}^S_{surf} dv,$$

$$\forall\mathcal{P} - F - \text{material}: \qquad \frac{d}{dt}\int\limits_{\mathcal{P}} \rho^F \eta^F dV + \int\limits_{\mathcal{P}} \operatorname{Div}\mathbf{H}^F dV = \int\limits_{\mathcal{P}} \hat{\eta}^F dV + \int\limits_{\mathcal{P}\cap\Sigma} \hat{\eta}^F_{surf} dv, \tag{3.4}$$

$$\eta^S = \eta^S(\mathcal{C}), \qquad \eta^F = \eta^F(\mathcal{C}), \qquad \mathbf{H}^S = \mathbf{H}^S(\mathcal{C}), \qquad \mathbf{H}^F = \mathbf{H}^F(\mathcal{C}). \tag{3.5}$$

It is assumed that at each point $X \in B\backslash\Sigma$ the following inequality

$$\hat{\eta}^S + \hat{\eta}^F \geq 0, \tag{3.6}$$

holds for all solutions of field equations.

By means of balance equations (3.4) it can be written in the local form

$$\frac{\partial}{\partial t}\left(\rho^S\eta^S + \rho^F\eta^F\right) + \operatorname{Div}\left(\rho^F\eta^F\acute{\mathbf{X}}^F + \mathbf{H}^S - \mathbf{H}^F\right) \geq 0. \tag{3.7}$$

This entropy inequality yields thermodynamical admissibility conditions which we discuss in the Appendix. For our further considerations we limit the attention to the model describing small deviations from the state of thermodynamical equilibrium. This state is defined within the present model as such for which the following conditions hold

$$\mathbf{G}|_E = 0, \quad \hat{\boldsymbol{\rho}}^S\big|_E = 0, \quad \hat{\mathbf{p}}^S\big|_E = 0, \quad \hat{n}|_E = 0. \tag{3.8}$$

Then as we show in the Appendix the following relations hold true

$$\acute{\mathbf{X}}\Big|_E = 0, \quad \Delta|_E = 0, \quad \Delta := n - n_E, \quad n_E = n_E\left(\frac{\rho^F}{\rho^S}\right), \tag{3.9}$$

and the basic constitutive relations are as follows. The intrinsic heat flux in both components defined by the sum of partial fluxes is independent of the relative velocity $\acute{\mathbf{X}}^F$, and of the change of porosity Δ, and it has the form

$$\begin{aligned} \mathbf{Q}^S + \mathbf{Q}^F &= -K_\Theta \mathbf{G} = \Theta\left(\mathbf{H}^S + \mathbf{H}^F\right), \\ K_\Theta &= K_\Theta\left(\mathcal{C}_E\right), \quad \mathcal{C}_E := \left\{\rho^F, \rho^S, \mathbf{F}^S, \Theta\right\} \end{aligned} \tag{3.10}$$

while the constitutive relation for the flux of porosity simplifies to a single constant

$$\mathbf{J} = \varphi J^S \acute{\mathbf{X}}^F, \quad \varphi = const. \tag{3.11}$$

This constant is determined for a particular initial state of the porous medium which means it may still be parametrically dependent on an initial porosity. This was indicated in earlier works on this model where it was argued that $\varphi \approx n_E$ for the constant equilibrium porosity n_E.

Under the restriction of processes to a small neighbourhood of the thermodynamical equilibrium the coupling through the partial Piola-Kirchhoff stress tensors reduces solely to the coupling through the dynamical change of porosity Δ

$$\begin{aligned} \mathbf{P}^S &= \rho^S \frac{\partial \psi^S}{\partial \mathbf{F}^S} - \Theta \Lambda_1^n \varphi J^S \Delta \mathbf{F}^{S-T}, \\ \mathbf{P}^F &= \left(-p^F + \Theta \Lambda_1^n \varphi \Delta\right) J^S \mathbf{F}^{S-T}, \quad p^F := \rho^{F2} \frac{\partial \psi^F}{\partial \rho^F} J^{S-1}, \end{aligned} \tag{3.12}$$

where

$$\begin{aligned} \psi^F &: = \varepsilon^F - \Theta \eta^F = \psi^F\left(\rho^F J^{S-1}, \Theta, \Delta\right), \\ \psi^S &: = \varepsilon^S - \Theta \eta^S = \psi^S\left(\rho^S, \mathbf{F}^S, \Theta, \Delta\right), \\ \Lambda_1^n &: = -\frac{1}{\Theta} \frac{\partial}{\partial \Delta}\left(\rho^S \psi^S + \rho^F \psi^F\right)\Big|_E . \end{aligned} \tag{3.13}$$

The free energies ψ^S, ψ^F contain solely two contributions. One is independent of Δ, the other one is quadratic in Δ, and, in addition,

$$\eta^F = -\frac{\partial \psi^F}{\partial \Theta}. \tag{3.14}$$

The sources are given by the relations

$$\hat{\mathbf{p}}^S = \pi\left(\acute{\mathbf{x}}^F - \acute{\mathbf{x}}^S\right) + \hat{\rho}^S \acute{\mathbf{x}}^S,$$

$$\hat{\rho}^S = R\left(\psi^F + \frac{p^F}{\rho^F J^{S-1}} - \psi^S - \rho^S \frac{\partial \psi^S}{\partial \rho^S}\right), \tag{3.15}$$

where the coefficients π, R may still depend on all equilibrium constitutive variables $\mathcal{C}_E$. Obviously, the formula for mass sources contains the difference of functions reminding the chemical potentials of the fluid $\psi^F + \frac{p^F}{\rho^F J^{S-1}}$, and of the skeleton $\psi^S + \rho^S \frac{\partial \psi^S}{\partial \rho^S}$. However, the second contribution to the potential of the skeleton does not coincide with the partial pressure (see: (3.12_1)) as ρ^S and $\mathbf{F}^S$ are independent.

Finally the following dissipation inequality must hold

$$\frac{1}{\Theta} K_\Theta \mathbf{G} \cdot \mathbf{G} + \pi\left(\acute{\mathbf{x}}^F - \acute{\mathbf{x}}^S\right) \cdot \left(\acute{\mathbf{x}}^F - \acute{\mathbf{x}}^S\right) + \frac{\partial}{\partial \Delta}\left(\rho^S \psi^S + \rho^F \psi^F\right)\Big|_E \frac{1}{\tau} \Delta^2 +$$

$$+R\left(\psi^F + \frac{p^F}{\rho^F J^{S-1}} - \psi^S - \rho^S \frac{\partial \psi^S}{\partial \rho^S}\right)^2 \geq 0. \tag{3.16}$$

This completes the general thermodynamical construction of the two component thermoporoelastic model.

In more general cases of multicomponent systems solely partial results on thermodynamical admissibility are available [6, 3].

Further in this work use as well the Eulerian description. The local balance equations and the thermodynamical results presented above have in this description the following form in a generic point $\mathbf{x} \in \mathbf{f}^S(B, t)$

mass balance

$$\begin{aligned} \frac{\partial \rho_t^S}{\partial t} + \operatorname{div}\left(\rho_t^S \mathbf{v}^S\right) &= \hat{\rho}_t^S, \quad \frac{\partial \rho_t^F}{\partial t} + \operatorname{div}\left(\rho_t^F \mathbf{v}^F\right) = -\hat{\rho}_t^S, \\ \rho_t^S &:= \rho^S J^{S-1}, \quad \rho_t^F := \rho^F J^{S-1}, \quad \hat{\rho}_t^S := \hat{\rho}^S J^{S-1}, \end{aligned}$$

$$\mathbf{v}^S := \acute{\mathbf{x}}^S\left(\mathbf{f}^{S-1}(\mathbf{x}, t), t\right), \quad \mathbf{v}^F := \acute{\mathbf{x}}^F\left(\mathbf{f}^{S-1}(\mathbf{x}, t), t\right), \tag{3.17}$$

and the operator div as well as grad in the following relations concern the Eulerian differentiation with respect to $\mathbf{x}$,

momentum balance

$$\begin{aligned} \rho_t^S\left(\frac{\partial \mathbf{v}^S}{\partial t} + \mathbf{v}^S \cdot \operatorname{grad} \mathbf{v}^S\right) &= \operatorname{div} \mathbf{T}^S + \hat{\mathbf{p}}_t^S - \hat{\rho}_t^S \mathbf{v}^S, \\ \mathbf{T}^S &:= J^{S-1} \mathbf{P}^S \mathbf{F}^{ST}, \quad \hat{\mathbf{p}}_t^S := J^{S-1} \hat{\mathbf{p}}^S, \\ \rho_t^F\left(\frac{\partial \mathbf{v}^F}{\partial t} + \mathbf{v}^F \cdot \operatorname{grad} \mathbf{v}^F\right) &= \operatorname{div} \mathbf{T}^F - \hat{\mathbf{p}}_t^S + \hat{\rho}_t^S \mathbf{v}^F, \\ \mathbf{T}^F &:= J^{S-1} \mathbf{P}^F \mathbf{F}^{ST}, \end{aligned} \tag{3.18}$$

energy balance

$$
\begin{aligned}
&\rho_t^S \left(\frac{\partial \varepsilon^S}{\partial t} + \mathbf{v}^S \cdot \operatorname{grad} \varepsilon^S \right) + \rho_t^F \left(\frac{\partial \varepsilon^F}{\partial t} + \mathbf{v}^F \cdot \operatorname{grad} \varepsilon^F \right) + \operatorname{div} \left(\mathbf{q}^S + \mathbf{q}^F \right) = \\
&= \mathbf{T}^S \cdot \operatorname{grad} \mathbf{v}^S + \mathbf{T}^F \cdot \operatorname{grad} \mathbf{v}^F + \\
&+ \hat{\rho}_t^S \left(\varepsilon^F - \varepsilon^S - \frac{1}{2} \left(\mathbf{v}^F - \mathbf{v}^S \right) \cdot \left(\mathbf{v}^F - \mathbf{v}^S \right) \right) + \left(\hat{\mathbf{p}}_t^S - \hat{\rho}_t^S \mathbf{v}^S \right) \cdot \left(\mathbf{v}^F - \mathbf{v}^S \right), \\
&\mathbf{q}^S := J^{S-1} \mathbf{F}^S \mathbf{Q}^S, \quad \mathbf{q}^F := J^{S-1} \mathbf{F}^S \mathbf{Q}^F,
\end{aligned}
\tag{3.19}
$$

balance of porosity

$$
\frac{\partial \Delta}{\partial t} + \mathbf{v}^S \cdot \operatorname{grad} \Delta + J^S \operatorname{div} \left(\varphi \left(\mathbf{v}^F - \mathbf{v}^S \right) \right) = \hat{n}. \tag{3.20}
$$

Apart from the mass sources we need solely linear constitutive laws, and these have the form

partial Cauchy stress tensors

$$
\begin{aligned}
\mathbf{T}^S &= \mathbf{T}_0^S + \lambda^S \mathbf{e}^S \cdot \mathbf{1}\mathbf{1} + 2\mu^S \mathbf{e}^S + \beta \Delta \mathbf{1}, \\
\mathbf{T}^F &= \left(-p^F - \beta \Delta \right) \mathbf{1}, \quad p^F = p_0^F + \kappa \left(\rho_t^F - \rho_0^F \right),
\end{aligned}
$$

$$
\beta := \frac{\partial}{\partial \Delta} \left(\rho_t^S \psi^S + \rho_t^F \psi^F \right) \bigg|_{\Delta = 0} \varphi, \tag{3.21}
$$

where $\mathbf{T}_0^S, p_0^F, \rho_0^F$ denote reference values of the Cauchy stress in the skeleton, partial pressure in the fluid, and the partial mass density of the fluid, respectively, λ^S, μ^S, κ are Lamé parameters of the skeleton, and the compressibility parameter of the fluid, respectively, and they may still be dependent on a reference porosity n_0; the small deformation of the skeleton $\mathbf{e}^S$ is as follows

$$
\mathbf{e}^S := \frac{1}{2} \left(\mathbf{1} - \mathbf{F}^{S-T} \mathbf{F}^{S-1} \right), \quad \left\| \mathbf{e}^S \right\| := \max \left(\left| \lambda^{(1)} \right|, \left| \lambda^{(2)} \right|, \left| \lambda^{(3)} \right| \right), \quad \left\| \mathbf{e}^S \right\| \ll 1, \tag{3.22}
$$

$\lambda^{(a)}, a = 1, 2, 3$ being the eigenvalues (principal stretches) of $\mathbf{e}^S$,

internal energies

$$
\begin{aligned}
\varepsilon^S &= \varepsilon^S \left(\rho_t^S, \mathbf{e}^S, \Theta, \Delta \right), \\
\varepsilon^F &= \varepsilon^F \left(\rho_t^F, \Theta, \Delta \right),
\end{aligned}
\tag{3.23}
$$

where the dependence on Δ is even, and at most quadratic,

the intrinsic heat flux

$$\mathbf{q}^S + \mathbf{q}^F = -\varkappa \operatorname{grad} \Theta, \quad \varkappa \approx K_\Theta, \tag{3.24}$$

the porosity source, and the equilibrium porosity

$$\hat{n} = -\frac{\Delta}{\tau}, \quad n_E = n_E\left(\frac{\rho_t^F}{\rho_t^S}\right), \quad \text{e.g.} \quad n_E = n_0 \frac{\rho_t^F}{\rho_0^F}\frac{\rho_0^S}{\rho_t^S}. \tag{3.25}$$

We skip here easy proofs of the above relations.

4 Mass exchange, adsorption

Macroscopic processes of mass exchange between components of mixtures of fluids, and solids belong to one of the three fundamental classes: phase changes, chemical reactions or adsorption/desorption processes. Within the first two classes the exchange of mass is accompanied by thermal effects due to the presence of a latent heat of reaction. The processes of the last class can be considered to be isothermal, for instance for a small concentration of adsorbate.

We skip here the presentation of phase changes. Let us only mention that theories of both diffusionless phase changes as well as these with diffusion (e.g. phase field theories) develop recently very vehemently.

Continuum models of diffusion processes with mass exchange are developed very well for mixtures of fluids. There is very little done for porous, and granular materials. Some work was done on combustion problems, and most of the results are based on the classical model of M. A. Goodwin and S. C. Cowin [7] (e.g. [8]). Difficulties are connected with the coupling of diffusion, and heat conduction. Particularly in processes in which one has to account for multiple temeperatures there is barely a progress at all.

In this work we limit our attention to adsorption processes and present a construction of the mass source contribution to mass balance equations of a three component continuous model of porous materials.

Adsorption belongs to the most important problems of practical bearing within theories of porous, and granular materials. This is connected primarily with a very large internal surface per unit volume in such materials on which the mass exchange takes place. For example 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 their external surface. This property is used in many technological processes. For instance in the growth of SiC single crystals by sublimation the vapour of silicium flows through a porous graphite wall in which it forms various carbite connections. A charcoal granular materials is also used in gas masks. Lungs, many filters and chemical reactors are made of porous materials for the same reason.

The model of such a mass exchange between a fluid component, and a solid in porous, and granular materials is based on the classical work of Langmuir (e.g. see the review in [9]). 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 Å = 50 nm - one can still rely on the assumption that the influence of the curvature of the surface is small.

On the microscopic level of description of porous, and granular materials we rely on the assumption that particles of the adsorbate change their kinematics from fluid to solid due to a weak van der Waals interaction with internal surfaces of the skeleton (a solid component of the system). The transfer of particles from the fluid component to the internal surface of the solid depends on a partial pressure of the fluid adsorbate, on an area of this surface, and on a number of available *bare sites* on this surface. The physical interpretation of the latter depends on the nature of adsorption processes on internal surfaces. On the macroscopic level (i.e. averaged over the *representative elementary volume (REV)* of a porous or granular material) the normalized fraction of these 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 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 transfered in unit time from the liquid phase to the solid skeleton is given by the balance relation

$$\hat{\rho}_t^A = -m^A \frac{d\,(xy)}{dt}, \qquad y := \frac{f_{int}}{V}, \tag{4.1}$$

where $\hat{\rho}_t^A$ denotes the intensity of mass source per unit time, and unit macroscopic volume in the current configuration.

In order to construct the model we have to specify the rates in this relation.

For $\frac{dx}{dt}$ we assume that changes of the fraction x are described by the Langmuir relation

$$\frac{dx}{dt} = a\,(1-x)\,p^A - bxe^{-\frac{E_b}{k\Theta}}, \tag{4.2}$$

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 Θ is the absolute temperature. In the case of full phase equilibrium we obtain from the equation (4.2) the following relation for the fraction of occupied sites

$$x = x_L := \frac{\frac{p^A}{p_0}}{1 + \frac{p^A}{p_0}}, \qquad p_0 := \frac{b}{a} e^{-\frac{E_b}{k\Theta}}, \tag{4.3}$$

which defines the so-called 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 $\frac{p^A}{p_0} \to \infty$. 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 nonequlibrium states which are described by the rate equation (4.2) and are connected with the dissipation.

In the mass source (4.1) 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 the volume of skeleton. This seems to be appropriate in processes of small deformations of the skeleton with accompanying small changes of the equilibrium porosity n_E. Then their influence on changes of internal surface can be neglected as being of the higher order than dissipative changes.

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

$$\frac{1}{y}\frac{dy}{dt} = \varsigma \frac{\hat{n}}{n}, \tag{4.4}$$

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 (4.3). Then the mass source (4.1) vanishes identically. The behavior of the continuous model based on the above assumptions has been checked on a simple bench-mark homogeneous problem [10]. It was found that results are indeed qualitatively in agreement with observations.

We present here the set of field equations which cover 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.

We use the Eulerian description of the system in which mass densities are referred to the current configuration. Then for the mass density of the skeleton, the fluid carrier of the adsorbate, and the adsorbate in the liquid state we have for $\mathbf{x} \in \mathbf{f}^S(B,t)$, $t \in T$

$$\rho_t^S := \rho^S J^{S-1}, \quad \rho_t^F := \rho^F J^{S-1}, \quad \rho_t^A := \rho^A J^{S-1}. \tag{4.5}$$

We consider solely isothermal processes. According to these remarks we have to determine the following fields

$$\left\{\rho_t^S, \rho_t^L, c, \mathbf{v}^S, \mathbf{e}^S, \mathbf{v}^F \equiv \mathbf{v}^A, n, x, y\right\}, \quad \rho_t^L := \rho_t^F + \rho_t^A, \tag{4.6}$$

where the concentration c is defined by the relation

$$c := \frac{\rho_t^A}{\rho_t^F + \rho_t^A} \ll 1. \tag{4.7}$$

Inspection of the list (4.6) reveals that the model contains, in addition to usual fields describing multicomponent systems, three microstructural fields: Δ, x, y. The first one describes changes of the microstructural geometry, and the remaining two - exchange of mass related to both energetic properties of the microstructure (the number of occupied sites x), and the geometry (the fraction of the internal surface y).

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. They have the form

mass balance

$$\begin{aligned} \frac{\partial \rho_t^S}{\partial t} + \operatorname{div}\left(\rho_t^S \mathbf{v}^S\right) &= -\rho_t^L \hat{c}, \quad \frac{\partial \rho_t^L}{\partial t} + \operatorname{div}\left(\rho_t^L \mathbf{v}^F\right) = \rho_t^L \hat{c}, \\ \frac{\partial c}{\partial t} + \mathbf{v}^F \cdot \operatorname{grad} c &= (1-c)\,\hat{c}, \quad \hat{c} := \frac{\hat{\rho}_t^A}{\rho_t^L} = -\frac{m^A}{\rho_0^L}\frac{d\,(xy)}{dt}, \end{aligned} \tag{4.8}$$

momentum balance

$$\frac{\partial \rho_t^L \mathbf{v}^F}{\partial t} + \operatorname{div}\left(\rho_t^L \mathbf{v}^F \otimes \mathbf{v}^F + p^L \mathbf{1}\right) + \pi\left(\mathbf{v}^F - \mathbf{v}^S\right) = 0$$

$$\rho_t^S \frac{\partial \mathbf{v}^S}{\partial t} = \operatorname{div}\mathbf{T}^S + \pi\left(\mathbf{v}^F - \mathbf{v}^S\right), \tag{4.9}$$

porosity balance

$$\frac{\partial \Delta}{\partial t} + \varphi \operatorname{div}\left(\mathbf{v}^F - \mathbf{v}^S\right) = -\frac{\Delta}{\tau},$$

where

$$\begin{aligned} \mathbf{T}^S &= \mathbf{T}_0^S + \lambda^S \operatorname{tr}\mathbf{e}^S \mathbf{1} + 2\mu^S \mathbf{e}^S + \beta\Delta\mathbf{1}, \\ p^L &= p_0^L + \varkappa\left(\rho_t^L - \rho_0^L\right) + \beta\Delta, \quad p^F = (1-c)\,p^L, \quad p^A = cp^L, \end{aligned} \tag{4.10}$$

with material parameters $\varphi, \lambda^S, \mu^S, \varkappa, \beta, \pi$ being constant. They depend parametrically on the constant initial porosity n_0. In addition we have

integrability condition

$$\frac{\partial \mathbf{e}^S}{\partial t} = \operatorname{sym}\operatorname{grad}\mathbf{v}^S, \tag{4.11}$$

evolution equations for microstructural variables

$$\begin{aligned} \frac{d \ln \frac{y}{y_0}}{dt} &= -\varsigma \frac{\Delta}{n_E}, \qquad y\,(t=0) = y_0 \equiv \frac{f_{int}\,(t=0)}{V}, \\ \frac{dx}{dt} &= \frac{1}{\tau_{ad}}\left[(1-x)\,\frac{cp^L}{p_0} - x\right], \quad x\,(t=0) = \frac{\frac{c_0 p_0^L}{p_0}}{1 + \frac{c_0 p_0^L}{p_0}}, \\ \tau_{ad} &:= \frac{1}{b} e^{\frac{E_b}{kT}}, \qquad c_0 := c\,(t=0). \end{aligned} \tag{4.12}$$

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 [9], and subsequent publications [11, 12, 13]. We quote here solely the most important conclusions of these works.

Investigation of a one dimensional flow of an ideal liquid through a poroelastic linear material has shown that the rate of adsorption depends on the magnitude of the relative velocity. This dependence is nonmonotonous. The rate is small for either small or very large relative velocities, and there appears a maximum of the rate at an intermediate velocity. Both position of this maximum as well as its amplitude depend on the time lapse from the beginning of the adsorption process. It has been also found out that an influence of changes of internal surface is limited to a very small neighbourhood of the initial instant of time. This is understandable as the relaxation time of porosity is much smaller than this of adsorption. Simultaneously it has been confirmed that an intensity of adsorption processes coupled to diffusion depends on the surface permeability which controls the relative velocity in the system. In the work in progress similar results seem to follow from a numerical analysis of a two dimensional problem.

5 Interfaces, ideal walls, boundary conditions

5.1 Introduction

Properties of interfaces in multicomponent systems with different kinematics of components are much more involved than these following from dynamical compatibility conditions of the usual continuum thermodynamics. This is related to the existence of boundary layers in transition regions between a porous body, and a neighbouring system (e.g. a fluid component flowing through a permeable boundary of the porous body to the exterior or another porous body with, maybe, different number of components which is the case if it is, for instance, not fully saturated). Boundary layers are replaced in the present model by singular surfaces, and these, as a consequence of these properties, must possess a structure of its own replacing gradients of fields in transition regions. This is the reason for introducing surface sources on material surfaces (interfaces of the skeleton) as we indicated in Section 2. We proceed to improve this motivation, and to investigate consequences of such improved conditions on the construction of thermodynamical properties of fields and boundary value problems.

One of such problems appears in a physical interpretation of the temperature. We limit the attention to the single temperature field common for all components as the problem for systems with multiple temperatures does not have a solution as yet.

The classical thermodynamical argument concerning the interpretation of the temperature is as follows. If we bring together two thermodynamical systems each of them being in the state of thermodynamical equilibrium, and the contact surface admits solely a nonmechanical flux of energy between them (i.e. the mechanical working of one system on the other is not allowed) then we say that these two systems are in thermodynamical equilibrium with each other if this nonmechanical flux vanishes. By constructing equivalence classes of such systems we introduce an empirical temperature as a scalar-valued function on the set of all systems which is the same for the systems in a thermodynamical equilibrium with each other. The classical considerations of the integrability of Gibbs equaltion lead then to the notion of the absolute temperature as a special choice of an empirical temperature. This argument is transferred to systems in which solely local thermodynamical equilibria appear. However, we can indeed consider local equilbria on interfaces if we can prove the continuity of the temperature in globally nonequilibrium processes. Such an argument is based in single component systems on dynamical compatibility conditions. Namely on a material surface of such a system the global energy, and entropy balances yield the continuity of the normal component of the heat flux, and of the entropy flux. Consequently, if these two fluxes are related to each other by a classical proportionality relation with the proportionality factor being equal to the inverse of the absolute temperature then it follows that the temperature must be continuous as well. Consequently if one of the systems is identified with a thermometer we can measure the temperature by the contact through the interface, and we can control the temperature on the boundary if we want to construct the boundary value problem for the heat conduction.

In the case of multicomponent systems permeable interfaces are not material for some components, and, consequently, partial heat and entropy fluxes are not continuous. The question arises if we can still use the classical argument on the continuity of the temperature, and, consequently, if we can construct boundary value problems in terms of the temperature for the heat conduction in such systems. We proceed to investigate this question.

5.2 Compatibility conditions on an interface

We consider a smooth orientable surface Σ, material with respect to the skeleton, i.e.

$$\Psi(\mathbf{X}) = 0, \qquad \mathbf{X} \in B, \qquad \mathbf{N} := \frac{\operatorname{Grad} \Psi}{|\operatorname{Grad} \Psi|} \tag{5.1}$$

where $\mathbf{N}$ is the unit normal vector specifying the positive and negative sides of the surface Σ. In its current configuration, this surface is described by the equation

$$\begin{aligned} &\psi(\mathbf{x}, t) := \Psi\Big(\mathbf{f}^{S^{-1}}(\mathbf{x}, t)\Big) = 0, \quad x \in \mathbf{f}^S(B, t) \\ \text{i.e.} \qquad &\mathbf{n} := \frac{\operatorname{grad} \psi}{|\operatorname{grad} \psi|} = \frac{\mathbf{F}^{S-T}\mathbf{N}}{|\mathbf{F}^{S-T}\mathbf{N}|}, \quad u = \acute{\mathbf{x}}^S \cdot \mathbf{n}, \end{aligned} \tag{5.2}$$

with $\mathbf{n}$ being the unit normal vector, and u is the normal speed of propagation of the image $\sigma := \mathbf{f}^S(\Sigma, t)$. The vector $\mathbf{n}$ is well defined due to the relation

$$[\![J^S \mathbf{F}^{S-T}\mathbf{N}]\!] = 0, \qquad [\![\ldots]\!] := (\ldots)^+ - (\ldots)^-, \tag{5.3}$$

which follows from the smoothness assumption. The brackets $(\ldots)^{+}$, $(\ldots)^{-}$ denote the positive and negative finite limits on the surface Σ.

Let us consider the balance equations reduced to this surface.

Mass balance
According to (2.6) in the absence of mass sources the jump of the mass density of skeleton $\llbracket \rho^S \rrbracket$ is not limited by the balance equations, and the jump of the mass density of the fluid must fulfil the condition

$$\forall_{\mathbf{X}\in\Sigma} \llbracket \rho^F \acute{\mathbf{X}}^F \rrbracket \cdot \mathbf{N} = 0 \implies \forall_{x\in\sigma} \llbracket \rho_t^F (\mathbf{v}^F - \mathbf{v}^S) \rrbracket \cdot \mathbf{n} = 0. \tag{5.4}$$

The latter relation in the current configuration shows that the mass flow of the fluid through the interface is continuous. The interface does not contain sinks.

Momentum balance
Due to the presence of surface sources in (2.8) we obtain in $\mathbf{X} \in \Sigma$

$$\llbracket \mathbf{P}^S \mathbf{N} \rrbracket - \hat{\mathbf{p}}^S_{surf} = 0, \qquad \left(\rho^F \acute{\mathbf{X}}^F \cdot \mathbf{N}\right) \llbracket \acute{\mathbf{x}}^F \rrbracket = \llbracket \mathbf{P}^F \rrbracket \mathbf{N} + \hat{\mathbf{p}}^F_{surf}, \tag{5.5}$$

or, in the Eulerian description, for $\mathbf{x} \in \sigma$

$$\begin{aligned} \llbracket \mathbf{T}^S \mathbf{n} \rrbracket + \hat{\mathsf{p}}^S_{surf} = 0, \qquad & \hat{\mathsf{p}}^S_{surf} := J^{S-1} \left|\mathbf{F}^{S-T}\mathbf{N}\right|^{-1} \hat{\mathbf{p}}^S_{surf} \\ \left(\rho_t^F (\mathbf{v}^F - \mathbf{v}^S) \cdot \mathbf{n}\right) \llbracket \mathbf{v}^F \rrbracket = - \llbracket \mathsf{p}^F \rrbracket \mathbf{n} + \hat{\mathsf{p}}^F_{surf}, \quad & \hat{\mathsf{p}}^F_{surf} := J^{S-1} \left|\mathbf{F}^{S-T}\mathbf{N}\right|^{-1} \hat{\mathbf{p}}^F_{surf} \end{aligned} \tag{5.6}$$

where we have used the constitutive assumption that the fluid is ideal (see: (3.12), $(3.21)_2$), i.e.

$$\mathbf{P}^F = J^S \mathbf{T}^F \mathbf{F}^{S-T} \equiv -J^S \mathsf{p}^F \mathbf{F}^{S-T}, \qquad \mathsf{p}^F := p^F + \beta\Delta. \tag{5.7}$$

Relation $(5.6)_2$ motivates the necessity of the surface sources of momentum. It has been argued (e. g. [3, 14, 15, 9]) that the boundary conditions on permeable boundaries of skeleton should follow from the bulk momentum balance

$$\left(\rho^F \acute{\mathbf{X}}^F \cdot \mathbf{N}\right) \llbracket \acute{\mathbf{x}}^F \rrbracket - \llbracket \mathbf{P}^F + \mathbf{P}^S \rrbracket \cdot \mathbf{N} \Big|_{\Sigma} = 0 \tag{5.8}$$

and from the flow condition for the fluid

$$\begin{aligned} \rho^F \acute{\mathbf{X}}^F \cdot \mathbf{N} \Big|_{\Sigma} &= \alpha_0 \left\llbracket J^{S-1} \frac{\mathbf{P}^F \cdot \mathbf{F}^S}{n} \right\rrbracket \Big|_{\Sigma} \implies \\ &\implies \rho_t^F \left(\mathbf{v}^F - \mathbf{v}^S\right) \cdot \mathbf{n} \Big|_{\sigma} = \alpha \left(p^{F-} - \frac{n^-}{n^+} p^{F+} \right) \Big|_{\sigma}, \\ &\qquad\qquad \alpha := \frac{3\alpha_0}{n^-} \left(\mathbf{N} \cdot \mathbf{C}^{S-1} \mathbf{N}\right)^{-1/2}, \end{aligned} \tag{5.9}$$

$$\acute{\mathbf{X}}^F - \acute{\mathbf{X}}^F \cdot \mathbf{NN}\Big|_{\Sigma} = 0, \tag{5.10}$$

where α is the so-called surface permeability coefficient. The condition (5.10) is characteristic for ideal fluids, and, if needed, can be replaced by a Beavers-Joseph type of a condition for the slip motion. In such a case the constitutive law for the partial stress $\mathbf{T}^F$ must be modified in order to include shear stresses (e.g. due to viscosity of the fluid component). Condition (5.9) states that the amount of fluid mass which flows through a permeable boundary is driven by the discontinuity of the pressure. It has been assumed that for relatively slow processes the pore pressure can be described by the simple relation $p = \frac{p^F}{n}$. Relation $(5.9)_2$ can be easily motivated on theoretical grounds. If one assumes that in a thin transition layer near the interface Σ a simple Darcy law holds true

$$-n \,\mathrm{grad}\, \frac{p^F}{n} - \pi(\mathbf{v}^F - \mathbf{v}^S) = 0, \tag{5.11}$$

then

$$\frac{\rho_t^F \langle n \rangle}{\pi L}\left[\!\!\left[\frac{p^F}{n}\right]\!\!\right] \approx \rho_t^F(\mathbf{v}^F - \mathbf{v}^S)\cdot\mathbf{n}, \qquad \langle n \rangle := \tfrac{1}{2}(n^+ + n^-), \tag{5.12}$$

where L is the thickness of the boundary layer. Relation (5.12) coincides, of course, with $(5.9)_2$ if $\alpha := \frac{\rho_t^F \langle n \rangle}{\pi L}$.

In the case of thermodynamical equilibrium we have $\acute{\mathbf{X}}^F \cdot \mathbf{N}\Big|_{\Sigma} = 0$ and relations $(5.6)_2$, and $(5.9)_2$ imply

$$[\![p^F]\!] + \hat{\mathsf{p}}^F_{surf} \cdot \mathbf{n}\Big|_{\sigma} = 0, \qquad \left[\!\!\left[\frac{p^F}{n}\right]\!\!\right]\Big|_{\sigma} = 0. \tag{5.13}$$

Consequently, if the source $\hat{\mathsf{p}}^F_{surf} \cdot \mathbf{n}\Big|_{\sigma}$ were zero the porosity n had to be continuous. This, certainly, cannot be the case.

The presence of the surface source of momentum can be easily understood in semimicroscopical terms. Various values of the surface permeability coefficient α yield a different distribution of the total load between solid and fluid components which is exerted by subbodies on each other through the interface Σ. Hence the partial pressure p^F cannot be continuous on Σ.

Energy balance
Bearing the global balance equations (2.10) in mind we obtain for $\mathbf{X} \in \Sigma$

$$\begin{aligned}
&\llbracket \mathbf{Q}^S \rrbracket \cdot \mathbf{N}\Big|_\Sigma = \llbracket \mathbf{P}^S \rrbracket \mathbf{N} \cdot \acute{\mathbf{x}}^S \Big|_\Sigma \equiv -\hat{\mathbf{p}}^S_{surf} \cdot \acute{\mathbf{X}}^S \Big|_\Sigma , \\
&\rho^F \acute{\mathbf{X}}^F \cdot \mathbf{N} \llbracket \varepsilon^F + \tfrac{1}{2} \acute{\mathbf{x}}^{F2} \rrbracket + \llbracket \mathbf{Q}^F \rrbracket \cdot \mathbf{N} \Big|_\Sigma = \llbracket (\mathbf{P}^F \mathbf{N}) \cdot \acute{\mathbf{X}}^F \rrbracket \Big|_\Sigma .
\end{aligned} \tag{5.14}$$

The second condition can be easily transformed to the following form

$$\begin{aligned}
&\rho^F \acute{\mathbf{X}}^F \cdot \mathbf{N} \llbracket \varepsilon^F + \tfrac{1}{2} (\acute{\mathbf{x}}^F - \acute{\mathbf{x}}^S) \cdot (\acute{\mathbf{x}}^F - \acute{\mathbf{x}}^S) \rrbracket \Big|_\Sigma + \llbracket \mathbf{Q}^F \rrbracket \cdot \mathbf{N} \Big|_\Sigma = \\
&= \llbracket (\mathbf{P}^F \mathbf{N}) \cdot (\acute{\mathbf{x}}^F - \acute{\mathbf{x}}^S) \rrbracket \Big|_\Sigma - \hat{\mathbf{p}}^F_{surf} \cdot \acute{\mathbf{x}}^F \Big|_\Sigma ,
\end{aligned} \tag{5.15}$$

where the momentum condition $(5.5)_2$ has been used. Consequently the bulk energy transport through the interface Σ can be written in the form

$$\llbracket \mathbf{Q}^S + \mathbf{Q}^F \rrbracket \cdot \mathbf{N} \Big|_\Sigma = -\rho^F \acute{\mathbf{X}}^F \cdot \mathbf{N} \left\llbracket \varepsilon^F - J^S \frac{p^F}{\rho^F} + \tfrac{1}{2} (\acute{\mathbf{x}}^F - \acute{\mathbf{x}}^S) \cdot (\acute{\mathbf{x}}^F - \acute{\mathbf{x}}^S) \right\rrbracket \Big|_\Sigma , \tag{5.16}$$

where the relation (5.7) has been applied. It is clear that the heat flux $(\mathbf{Q}^S + \mathbf{Q}^F) \cdot \mathbf{N}$ is not continuous on permeable boundaries.

Entropy balance
The global partial entropy balance equations

$$\begin{aligned}
&\forall \mathrm{P} \text{ - S-material}: \quad \frac{d}{dt} \int_{\mathcal{P}} \rho^S \eta^S dV + \oint_{\partial \mathcal{P}} \mathbf{H}^S \cdot \mathbf{N} dA = \int_{\mathcal{P}} \hat{\eta}^S dV + \oint_{\partial \mathcal{P}} \hat{\eta}^S_{surf} dA, \\
&\forall \mathrm{P} \text{ - F-material}: \quad \frac{d}{dt} \int_{\mathcal{P}} \rho^F \eta^F dV + \oint_{\partial \mathcal{P}} \mathbf{H}^F \cdot \mathbf{N} dA = \int_{\mathcal{P}} \hat{\eta}^F dV + \oint_{\partial \mathcal{P}} \hat{\eta}^F_{surf} dA
\end{aligned} \tag{5.17}$$

yield for the interface

$$\begin{aligned}
\left[\left[\mathbf{H}^S\right]\right] \cdot \mathbf{N}|_\Sigma &= \hat{\eta}^S_{surf}, \\
\rho^F \acute{\mathbf{X}}^F \cdot \mathbf{N} \left[\left[\eta^F\right]\right]\big|_\Sigma + \left[\left[\mathbf{H}^F\right]\right] \cdot \mathbf{N}|_\Sigma &= \hat{\eta}^F_{surf}.
\end{aligned} \tag{5.18}$$

Hence the intrinsic bulk transport of the entropy through the interface satisfies the relation

$$\left[\left[\mathbf{H}^S + \mathbf{H}^F + \rho^F \eta^F \acute{\mathbf{X}}^F\right]\right] \cdot \mathbf{N} \Big|_\Sigma = \hat{\eta}^S_{surf} + \hat{\eta}^F_{surf}. \tag{5.19}$$

We combine this result with the relation (5.16) for the intrinsic bulk transport of energy. Bearing relation $(3.10)_1$ in mind we obtain

$$\begin{aligned} &\rho^F \acute{\mathbf{X}}^F \cdot \mathbf{N} \left[\left[\varepsilon^F - J^S \frac{p^F}{\rho^F} - \Theta \eta^F \right]\right]\Bigg|_\Sigma = \\ &= -\left[\left[\Theta\right]\right] \left\langle \mathbf{H}^S + \mathbf{H}^F + \rho^F \eta^F \acute{\mathbf{X}}^F \right\rangle \cdot \mathbf{N}\Bigg|_\Sigma + \hat{\eta}^S_{surf} + \hat{\eta}^F_{surf}, \end{aligned} \tag{5.20}$$

where $2\left\langle \cdots \right\rangle = (\cdots)^+ + (\cdots)^-$, i.e. it is an average value on the interface, and we neglected the quadratic contribution of the relative velocity. This is justified as the relation $(3.10)_1$ was derived under the assumption of the small deviation from the state of thermodynamical equilibrium.

In the classical thermodynamics the problem of continuity of the absolute temperature is considered on the so-called *ideal walls* (see: I. Müller [im1]). The existence of ideal walls is required if we want temperature to be a measurable quantity[1]. Then entropy productions on such a surface are zero. If we make this assumption for the interface Σ then the absolute temperature Θ is continuous on this surface if it is either impermable or if the Gibbs free energy of the fluid component (chemical potential) is continuous

$$\left[\left[\mu^F\right]\right] = 0, \quad \mu^F := \varepsilon^F - J^S \frac{p^F}{\rho^F} - \Theta \eta^F. \tag{5.21}$$

This condition seems to be plausible because the density of the true Gibbs free energy of the fluid component μ^{FR} is approximately equal to μ^F due to the relation between the true mass density ρ^{FR}, and the partial mass density ρ^F: $\rho^F = n\rho^{FR}$. Hence the assumption on a local thermodynamical equilibrium yielding the continuity of μ^{FR} leads to the continuity of μ^F.

The above considerations show that processes arbitrarily deviated from the state of thermodynamical equilibrium yield problems with the operational definition of temperature. In such processes one cannot expect that surface entropy sources vanish. They are most likely of the second order in nonequilibrium variables, and, consequently remain in the jump condition. The requirement of continuity of the true chemical potential is not fulfilled either because one has to account for convective contributions in both energy, and entropy jump conditions.

We complete the considerations for interfaces material with respect to the skeleton with the analysis of porosity equation. From (2.11) we obtain easily

$$\left[\left[\varphi J^S \acute{\mathbf{X}}^F \cdot \mathbf{N}\right]\right] \equiv \rho^F \acute{\mathbf{X}}^F \cdot \mathbf{N} \left[\left[\frac{\varphi}{\rho^F J^{S-1}} \right]\right] = \hat{n}_{surf}, \tag{5.22}$$

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[1] Another example of such a wall for the transport of mass rather than energy is the *semipermeable membrane* of the mixture of fluids on which the chemical potential is continuous.

where relation (3.11) has been used.

Obviously the above relation could not be satisfied on an interface between two different porous materials for which $[[\varphi]] \neq 0$ if the initial porosity of both bodies was different, and the surface source of porosity was zero. Note that quantities appearing on the left hand side are all specified either by the initial conditions or by a solution of field equations. On the other hand field equations do not contain contributions of $\hat{n}_{surf}$. Consequently relation (5.24) can be considered to be the definition of this source.

Let us mention in passing that surface sources $\hat{\mathbf{p}}^{S}_{surf}, \hat{n}_{surf}$ are not needed for consistency of the model if the surface is not material, e.g. in the case of shock waves. In those cases the usual dynamical compatibility conditions yielding Rankine-Hugoniot conditions preserve their validity. The presence of sources is strictly related to a material change of microstructure on an interface between two different porous materials.

6 Conclusions

New results presented in this work concern two topics: a relation between partial fluxes of heat, and entropy following from the second law of thermodynamics, and relations on permeable interfaces separating a porous material from a single component system or a different porous material.

We have shown that the assumption on small deviations from thermodynamical equilibrium, i.e.

$$\max\left\{\|\mathbf{G}\|, \left\|\acute{\mathbf{X}}^{F}\right\|, \|\Delta\|\right\} \ll 1, \tag{6.1}$$

where the norms are chosen as supremum norms on $B \times T$, yields an explicit answer to the first question in the following form

$$\mathbf{H}^{S} + \mathbf{H}^{F} = \frac{\mathbf{Q}^{S} + \mathbf{Q}^{F}}{\Theta}, \quad \mathbf{J} = \varphi J^{S} \acute{\mathbf{X}}^{F}, \tag{6.2}$$

where $\mathbf{Q}^{S} + \mathbf{Q}^{F}$ is independent of $\acute{\mathbf{X}}^{F}$, and $\mathbf{J}$ is independent of $\mathbf{G}$.

Under the same assumption, and under the condition of local equilibrium of the fluid component on interfaces (i.e. the continuity of the chemical potential of the fluid component) we have shown that the absolute temperature is continuous on such interfaces.

These results allow to extend the model of poroelastic materials which has been investigated in earlier contributions to nonisothermal processes.

Apart from these two important results we have shown that the couplings between two components reduce also in a considerable manner under the condition of small deviations from the state of thermodynamical equilibrium. Namely we have shown that partial Cauchy stresses in the skeleton cannot depend on the current mass density of the fluid, and, *vice versa*, partial Cauchy stresses in the fluid depend solely on the current partial mass density of the fluid, and on the deviation of porosity Δ, but not on deformations of the skeleton. It means that in the linear simplified version of the model we do not obtain the Biot's multicomponent model of porous materials. However, in spite of some claims in the literature, this difference has solely a quantitative influence on properties of weak discontinuity waves, but it does not influence either the number of modes or their basic properties. This was in a way expected if one inspected carefully the analysis of wave propagation in mixtures of fluids. In the case of so-called ideal mixtures (no interaction terms in partial free energies) the number of modes remains the same as in the case of interacting mixtures, and only the speeds of propagation change a little.

Finally let us note that there is an indication that mass exchange processes yield their own contributions to stresses in the skeleton independent of the deformation. Namely in contrast to the fluid, for which the definition of the chemical potential contains the partial pressure divided by the mass density $\frac{p^F}{\rho^F J^{S-1}}$, the chemical potential coupled to mass source for the skeleton contains the contribution $\rho^S \frac{\partial \psi^S}{\partial \rho^S}$, rather than $-\frac{\operatorname{tr}\mathbf{T}^S}{3\rho^S J^{S-1}}$ which would be a usual partial pressure contribution in the skeleton. It means that the presence of mass exchange yields additional stress effects in the skeleton which would appear even in the case of lack of deformations of the skeleton.

7 Appendix: Evaluation of the entropy inequality

In this Appendix we evaluate solutions of the local entropy inequality. As usual in thermodynamics field equations are considered to be constraints imposed on the class of smooth solutions of the inequality. These constraint conditions are eliminated by Lagrange multipliers [16, 5]. Hence we have for all sufficiently smooth fields (2.5)

$$\rho^S \frac{\partial \eta^S}{\partial t} + \rho^F \frac{\partial \eta^F}{\partial t} + \rho^F \acute{\mathbf{X}}^F \cdot \operatorname{Grad} \eta^F + \operatorname{Div}\left(\mathbf{H}^S + \mathbf{H}^F\right) -$$

$$-\Lambda^S \frac{\partial \rho^S}{\partial t} - \Lambda^F \left(\frac{\partial \rho^F}{\partial t} + \acute{\mathbf{X}}^F \cdot \operatorname{Grad} \rho^F + \rho^F \operatorname{Div} \acute{\mathbf{X}}^F \right) -$$

$$-\mathbf{\Lambda}^{v^S} \cdot \left(\rho^S \frac{\partial \acute{\mathbf{x}}^S}{\partial t} - \operatorname{Div} \mathbf{P}^S \right) -$$

$$-\mathbf{\Lambda}^{v^F} \cdot \left(\rho^F \left(\frac{\partial \acute{\mathbf{x}}^F}{\partial t} + \acute{\mathbf{X}}^F \cdot \operatorname{Grad} \acute{\mathbf{x}}^F \right) - \operatorname{Div} \mathbf{P}^F \right) -$$

$$\begin{aligned}
&\quad -\Lambda^{\varepsilon}\left(\rho^S\frac{\partial \varepsilon^S}{\partial t}+\rho^F\left(\frac{\partial \varepsilon^F}{\partial t}+\acute{\mathbf{X}}^F\cdot\operatorname{Grad}\varepsilon^F\right)+\right.\\
&\quad \left.+\operatorname{Div}\left(\mathbf{Q}^S+\mathbf{Q}^F\right)-\mathbf{P}^S\cdot\operatorname{Grad}\acute{\mathbf{x}}^S-\mathbf{P}^F\cdot\operatorname{Grad}\acute{\mathbf{x}}^F\right)-\\
&-\Lambda^n\left(\frac{\partial n}{\partial t}+\operatorname{Div}\mathbf{J}\right)-\boldsymbol{\Lambda}^F\cdot\left(\frac{\partial \mathbf{F}^S}{\partial t}-\operatorname{Grad}\acute{\mathbf{x}}^S\right)+\\
&+\hat{\rho}^S\left(\eta^S-\eta^F\right)+\hat{\rho}^S\left(\Lambda^S-\Lambda^F\right)+\\
&+\left(\boldsymbol{\Lambda}^{v^S}-\boldsymbol{\Lambda}^{v^F}\right)\cdot\left(\hat{\mathbf{p}}^S-\hat{\rho}^S\acute{\mathbf{x}}^S\right)-\\
&-\Lambda^{\varepsilon}\left(-\hat{\mathbf{p}}^S\cdot\left(\acute{\mathbf{x}}^F-\acute{\mathbf{x}}^S\right)+\hat{\rho}^S\left(\varepsilon^S-\frac{1}{2}\acute{x}^{S2}-\varepsilon^F+\frac{1}{2}\acute{x}^{F2}\right)\right)+\\
&+\Lambda^n\hat{n}\geq 0. \qquad \text{(A.1)}
\end{aligned}$$

where the multipliers $\Lambda^S, \Lambda^F, \boldsymbol{\Lambda}^F, \boldsymbol{\Lambda}^{v^S}, \boldsymbol{\Lambda}^{v^F}, \Lambda^{\varepsilon}, \Lambda^n$ are constitutive functions continuously differentiable with respect to constitutive variables almost everywhere on the domain $B \times T$.

We have replaced the field of motion of the skeleton $\mathbf{f}^S$ by the field of deformation gradient $\mathbf{F}^S$, and the field of velocity $\acute{\mathbf{x}}^S$. Then the new fields must satisfy the following compatibility conditions in almost all points of the domain B

$$\frac{\partial \mathbf{F}^S}{\partial t}=\operatorname{Grad}\acute{\mathbf{x}}^S, \quad \operatorname{Grad}\mathbf{F}^S=\left(\operatorname{Grad}\mathbf{F}^S\right)^{\overset{23}{T}}. \qquad \text{(A.2)}$$

We account for the first condition in the same way as we do in the case of all other field equations, while the second one shall be directly substituted in thermodynamical relations.

It is easy to see that application of constitutive relations (3.3) yields a linearity of the above inequality with respect to the following derivatives

time derivatives

$$\left\{\frac{\partial \rho^S}{\partial t},\frac{\partial \rho^F}{\partial t},\frac{\partial \mathbf{F}^S}{\partial t},\frac{\partial n}{\partial t},\frac{\partial \Theta}{\partial t},\frac{\partial \mathbf{G}}{\partial t},\frac{\partial \acute{\mathbf{x}}^S}{\partial t},\frac{\partial \acute{\mathbf{x}}^F}{\partial t}\right\}, \qquad \text{(A.3)}$$

spatial derivatives

$$\left\{\operatorname{Grad}\rho^S, \operatorname{Grad}\rho^F, \operatorname{Grad}\mathbf{F}^S, \operatorname{Grad}n, \operatorname{Grad}\mathbf{G}, \operatorname{Grad}\acute{\mathbf{x}}^S, \operatorname{Grad}\acute{\mathbf{x}}^F\right\}. \tag{A.4}$$

This means that coefficients of these derivatives must vanish identically, and we obtain the following set of relations determining Lagrange multipliers

$$\Lambda^S = \rho^S\left(\frac{\partial\eta^S}{\partial\rho^S} - \Lambda^\varepsilon\frac{\partial\varepsilon^S}{\partial\rho^S}\right) + \rho^F\left(\frac{\partial\eta^F}{\partial\rho^S} - \Lambda^\varepsilon\frac{\partial\varepsilon^F}{\partial\rho^S}\right),$$

$$\Lambda^F = \rho^S\left(\frac{\partial\eta^S}{\partial\rho^F} - \Lambda^\varepsilon\frac{\partial\varepsilon^S}{\partial\rho^F}\right) + \rho^F\left(\frac{\partial\eta^F}{\partial\rho^F} - \Lambda^\varepsilon\frac{\partial\varepsilon^F}{\partial\rho^F}\right),$$

$$\mathbf{\Lambda}^F = \rho^S\left(\frac{\partial\eta^S}{\partial\mathbf{F}^S} - \Lambda^\varepsilon\frac{\partial\varepsilon^S}{\partial\mathbf{F}^S}\right) + \rho^F\left(\frac{\partial\eta^F}{\partial\mathbf{F}^S} - \Lambda^\varepsilon\frac{\partial\varepsilon^F}{\partial\mathbf{F}^S}\right),$$

$$\Lambda^n = \rho^S\left(\frac{\partial\eta^S}{\partial n} - \Lambda^\varepsilon\frac{\partial\varepsilon^S}{\partial n}\right) + \rho^F\left(\frac{\partial\eta^F}{\partial n} - \Lambda^\varepsilon\frac{\partial\varepsilon^F}{\partial n}\right),$$

$$0 = \rho^S\left(\frac{\partial\eta^S}{\partial\Theta} - \Lambda^\varepsilon\frac{\partial\varepsilon^S}{\partial\Theta}\right) + \rho^F\left(\frac{\partial\eta^F}{\partial\Theta} - \Lambda^\varepsilon\frac{\partial\varepsilon^F}{\partial\Theta}\right),$$

$$0 = \rho^S\left(\frac{\partial\eta^S}{\partial\mathbf{G}} - \Lambda^\varepsilon\frac{\partial\varepsilon^S}{\partial\mathbf{G}}\right) + \rho^F\left(\frac{\partial\eta^F}{\partial\mathbf{G}} - \Lambda^\varepsilon\frac{\partial\varepsilon^F}{\partial\mathbf{G}}\right),$$

$$\rho^S\mathbf{\Lambda}^{v^S} = -\mathbf{F}^{S-T}\left\{\rho^S\left(\frac{\partial\eta^S}{\partial\acute{\mathbf{X}}^F} - \Lambda^\varepsilon\frac{\partial\varepsilon^S}{\partial\acute{\mathbf{X}}^F}\right) + \rho^F\left(\frac{\partial\eta^F}{\partial\acute{\mathbf{X}}^F} - \Lambda^\varepsilon\frac{\partial\varepsilon^F}{\partial\acute{\mathbf{X}}^F}\right)\right\},$$

$$\rho^F\mathbf{\Lambda}^{v^F} = \mathbf{F}^{S-T}\left\{\rho^S\left(\frac{\partial\eta^S}{\partial\acute{\mathbf{X}}^F} - \Lambda^\varepsilon\frac{\partial\varepsilon^S}{\partial\acute{\mathbf{X}}^F}\right) + \rho^F\left(\frac{\partial\eta^F}{\partial\acute{\mathbf{X}}^F} - \Lambda^\varepsilon\frac{\partial\varepsilon^F}{\partial\acute{\mathbf{X}}^F}\right)\right\}, \tag{A.5}$$

in the case of coefficients of time derivatives, and the identities limiting constitutive relations

$$\frac{\partial\left(\mathbf{H}^S + \mathbf{H}^F\right)}{\partial\rho^S} - \Lambda^\varepsilon\frac{\partial\left(\mathbf{Q}^S + \mathbf{Q}^F\right)}{\partial\rho^S} - \Lambda^n\frac{\partial\mathbf{J}}{\partial\rho^S} +$$

$$+\rho^F\acute{\mathbf{X}}^F\left(\frac{\partial\eta^F}{\partial\rho^S} - \Lambda^\varepsilon\frac{\partial\varepsilon^F}{\partial\rho^S}\right) + \left(\frac{\partial\mathbf{P}^S}{\partial\rho^S}\right)^T\mathbf{\Lambda}^{v^S} + \left(\frac{\partial\mathbf{P}^F}{\partial\rho^S}\right)^T\mathbf{\Lambda}^{v^F} = 0,$$

$$\frac{\partial\left(\mathbf{H}^S + \mathbf{H}^F\right)}{\partial\rho^F} - \Lambda^\varepsilon\frac{\partial\left(\mathbf{Q}^S + \mathbf{Q}^F\right)}{\partial\rho^F} - \Lambda^n\frac{\partial\mathbf{J}}{\partial\rho^F} - \Lambda^F\acute{\mathbf{X}}^F +$$

$$+\rho^F \acute{\mathbf{X}}^F \left(\frac{\partial \eta^F}{\partial \rho^F} - \Lambda^\varepsilon \frac{\partial \varepsilon^F}{\partial \rho^F}\right) + \left(\frac{\partial \mathbf{P}^S}{\partial \rho^F}\right)^T \boldsymbol{\Lambda}^{v^S} + \left(\frac{\partial \mathbf{P}^F}{\partial \rho^F}\right)^T \boldsymbol{\Lambda}^{v^F} = 0,$$

$$\overset{23}{\mathrm{sym}}\left\{\left[\frac{\partial\left(\mathbf{H}^S+\mathbf{H}^F\right)}{\partial \mathbf{F}^S}\right]^{\overset{12}{T}} - \Lambda^\varepsilon \left[\frac{\partial\left(\mathbf{Q}^S+\mathbf{Q}^F\right)}{\partial \mathbf{F}^S}\right]^{\overset{12}{T}} - \Lambda^n \left(\frac{\partial \mathbf{J}}{\partial \mathbf{F}^S}\right)^{\overset{12}{T}} + \right.$$

$$+\rho^F \Lambda^F \mathbf{F}^{S-T} \otimes \acute{\mathbf{X}}^F + \rho^F \left(\frac{\partial \eta^F}{\partial \mathbf{F}^S} - \Lambda^\varepsilon \frac{\partial \varepsilon^F}{\partial \mathbf{F}^S}\right) \otimes \acute{\mathbf{X}}^F + \tag{A.6}$$

$$\left. + \left[\left(\frac{\partial \mathbf{P}^S}{\partial \mathbf{F}^S}\right)^{\overset{14}{T}} \boldsymbol{\Lambda}^{v^S}\right]^{\overset{12}{T}} + \left[\left(\frac{\partial \mathbf{P}^F}{\partial \mathbf{F}^S}\right)^{\overset{14}{T}} \boldsymbol{\Lambda}^{v^F}\right]^{\overset{12}{T}} \right\} = 0,$$

$$\frac{\partial\left(\mathbf{H}^S+\mathbf{H}^F\right)}{\partial n} - \Lambda^\varepsilon \frac{\partial\left(\mathbf{Q}^S+\mathbf{Q}^F\right)}{\partial n} - \Lambda^n \frac{\partial \mathbf{J}}{\partial n} +$$

$$+\rho^F \acute{\mathbf{X}}^F \left(\frac{\partial \eta^F}{\partial n} - \Lambda^\varepsilon \frac{\partial \varepsilon^F}{\partial n}\right) + \left(\frac{\partial \mathbf{P}^S}{\partial n}\right)^T \boldsymbol{\Lambda}^{v^S} + \left(\frac{\partial \mathbf{P}^F}{\partial n}\right)^T \boldsymbol{\Lambda}^{v^F} = 0,$$

$$\mathrm{sym}\left\{\frac{\partial\left(\mathbf{H}^S+\mathbf{H}^F\right)}{\partial \mathbf{G}} - \Lambda^\varepsilon \frac{\partial\left(\mathbf{Q}^S+\mathbf{Q}^F\right)}{\partial \mathbf{G}} - \Lambda^n \frac{\partial \mathbf{J}}{\partial \mathbf{G}} + \right.$$

$$\left. +\rho^F \left(\frac{\partial \eta^F}{\partial \mathbf{G}} - \Lambda^\varepsilon \frac{\partial \varepsilon^F}{\partial \mathbf{G}}\right) \otimes \acute{\mathbf{X}}^F + \left(\frac{\partial \mathbf{P}^S}{\partial \mathbf{G}}\right)^{\overset{13}{T}} \boldsymbol{\Lambda}^{v^S} + \left(\frac{\partial \mathbf{P}^F}{\partial \mathbf{G}}\right)^{\overset{13}{T}} \boldsymbol{\Lambda}^{v^F} \right\} = 0,$$

as well as implicit relations for partial stresses

$$\Lambda^\varepsilon \mathbf{P}^S =$$

$$= -\boldsymbol{\Lambda}^F + \mathbf{F}^{S-T} \left\{ \left[\frac{\partial\left(\mathbf{H}^S+\mathbf{H}^F\right)}{\partial \acute{\mathbf{X}}^F}\right]^{\overset{12}{T}} - \Lambda^\varepsilon \left[\frac{\partial\left(\mathbf{Q}^S+\mathbf{Q}^F\right)}{\partial \acute{\mathbf{X}}^F}\right]^{\overset{12}{T}} - \Lambda^n \left(\frac{\partial \mathbf{J}}{\partial \acute{\mathbf{X}}^F}\right)^{\overset{12}{T}} - \right.$$

$$\left. -\rho^F \Lambda^F \mathbf{1} + \rho^F \left(\frac{\partial \eta^F}{\partial \acute{\mathbf{X}}^F} - \Lambda^\varepsilon \frac{\partial \varepsilon^F}{\partial \acute{\mathbf{X}}^F}\right) \otimes \acute{\mathbf{X}}^F + \left(\frac{\partial \mathbf{P}^S}{\partial \acute{\mathbf{X}}^F}\right)^{\overset{13}{T}} \boldsymbol{\Lambda}^{v^S} + \left(\frac{\partial \mathbf{P}^F}{\partial \acute{\mathbf{X}}^F}\right)^{\overset{13}{T}} \boldsymbol{\Lambda}^{v^F} \right\},$$

$$\Lambda^\varepsilon \mathbf{P}^F =$$

$$= \mathbf{F}^{S-T} \left\{ \rho^F \Lambda^F \mathbf{1} - \left[\frac{\partial \left(\mathbf{H}^S + \mathbf{H}^F \right)}{\partial \acute{\mathbf{X}}^F} \right]^{\overset{12}{T}} + \Lambda^\varepsilon \left[\frac{\partial \left(\mathbf{Q}^S + \mathbf{Q}^F \right)}{\partial \acute{\mathbf{X}}^F} \right]^{\overset{12}{T}} + \Lambda^n \left(\frac{\partial \mathbf{J}}{\partial \acute{\mathbf{X}}^F} \right)^{\overset{12}{T}} + \right.$$

$$\left. - \rho^F \left(\frac{\partial \eta^F}{\partial \acute{\mathbf{X}}^F} - \Lambda^\varepsilon \frac{\partial \varepsilon^F}{\partial \acute{\mathbf{X}}^F} \right) \otimes \acute{\mathbf{X}}^F - \left(\frac{\partial \mathbf{P}^S}{\partial \acute{\mathbf{X}}^F} \right)^{\overset{13}{T}} \mathbf{\Lambda}^{v^S} - \left(\frac{\partial \mathbf{P}^F}{\partial \acute{\mathbf{X}}^F} \right)^{\overset{13}{T}} \mathbf{\Lambda}^{v^F} \right\}, \qquad \text{(A.7)}$$

in the case of coefficients of spatial derivatives.

There remains the residual inequality which determines the dissipation D

$$D := \left\{ \frac{\partial \left(\mathbf{H}^S + \mathbf{H}^F \right)}{\partial \Theta} - \Lambda^\varepsilon \frac{\partial \left(\mathbf{Q}^S + \mathbf{Q}^F \right)}{\partial \Theta} - \Lambda^n \frac{\partial \mathbf{J}}{\partial \Theta} - \right.$$

$$\left. + \rho^F \acute{\mathbf{X}}^F \left(\frac{\partial \eta^F}{\partial \Theta} - \Lambda^\varepsilon \frac{\partial \varepsilon^F}{\partial \Theta} \right) + \left(\frac{\partial \mathbf{P}^S}{\partial \Theta} \right)^T \mathbf{\Lambda}^{v^S} + \left(\frac{\partial \mathbf{P}^F}{\partial \Theta} \right)^T \mathbf{\Lambda}^{v^F} \right\} \cdot \mathbf{G} +$$

$$+ \hat{\rho}^S \left\{ \eta^S + \Lambda^S - \Lambda^\varepsilon \left(\varepsilon^S - \frac{1}{2} \acute{x}^{S2} \right) - \eta^F - \Lambda^F + \Lambda^\varepsilon \left(\varepsilon^F - \frac{1}{2} \acute{x}^{F2} \right) \right\} +$$

$$+ \left(\mathbf{\Lambda}^{v^S} - \mathbf{\Lambda}^{v^F} \right) \cdot \left(\hat{\mathbf{p}}^S - \hat{\rho}^S \acute{\mathbf{x}}^S \right) + \mathbf{\Lambda}^{v^F} \cdot \hat{\rho}^S \left(\acute{\mathbf{x}}^F - \acute{\mathbf{x}}^S \right) +$$

$$+ \Lambda^\varepsilon \hat{\mathbf{p}}^S \cdot \left(\acute{\mathbf{x}}^F - \acute{\mathbf{x}}^S \right) + \Lambda^n \hat{n} \geq 0. \qquad \text{(A.8)}$$

We have made use of local balance equations for sources.

Apparently the dissipation D has the minimum in the state in which it is zero. Such a state is called the state of thermodynamical equilibrium. It appears if all three sources $\hat{\rho}^S, \hat{\mathbf{p}}^S, \hat{n}$, and the temperature gradient $\mathbf{G}$ are zero. For sufficiently smooth constitutive relations it means that D must be at least of the second order with respect to deviations from this state, and these are described by the gradient $\mathbf{G}$ again, the difference of chemical potentials of both components whose prototype appears as a coefficient of the mass source in (A.8), the relative velocity represented by the Lagrangian velocity $\acute{\mathbf{X}}^F \equiv \mathbf{F}^{S-1} \left(\acute{\mathbf{x}}^F - \acute{\mathbf{x}}^S \right)$, and by the deviation of the porosity n from its equilibrium value n_E:

$$\Delta := n - n_E, \quad n_E = n_E \left(\mathcal{C}_E \right), \quad \mathcal{C}_E := \left\{ \rho^F, \rho^S, \mathbf{F}^S, \Theta \right\} \qquad \text{(A.9)}$$

The constitutive relation for the equilibrium porosity n_E contains solely those constitutive variables whose values in the state of equilibrium are different from zero.

This structure indicates simplifications for processes with small deviations from the state of thermodynamical equilibrium.

Substitution of the definition (A.9) in the balance equation of porosity $(2.12)_7$ yields

$$\frac{\partial n_E}{\partial t} = 0, \quad \frac{\partial \Delta}{\partial t} + \operatorname{Div} \mathbf{J} = \hat{n}, \tag{A.10}$$

provided the deviation Δ is small. We have used the fact that the source of porosity must vanish in the state of thermodynamical equilibrium.

Bearing the constitutive relation for n_E in mind we obtain

$$\left(\frac{\partial n_E}{\partial \rho^S} - \frac{\partial n_E}{\partial \rho^F}\right) \hat{\rho}^S + \frac{\partial n_E}{\partial \mathbf{F}^S} \cdot \frac{\partial \mathbf{F}^S}{\partial t} + \frac{\partial n_E}{\partial \Theta} \frac{\partial \Theta}{\partial t} = 0. \tag{A.11}$$

where we have applied mass balance equations in the case $\acute{\mathbf{X}}^F = 0$ (equilibrium!).

The first term in this relation vanishes in equilibrium, and, consequently, n_E can be an arbitrary function of mass densities. On the other hand, neither $\frac{\partial \mathbf{F}^S}{\partial t}$ nor $\frac{\partial \Theta}{\partial t}$ are identically zero in equilibrium, and they may have locally arbitrary values. Consequently their coefficients being independent of those derivatives must be identically zero, and we finally obtain

$$n_E = n_E\left(\rho^S, \rho^F\right). \tag{A.12}$$

Dimensional analysis leads then to the conclusion that the equilibrium porosity n_E is solely a function of the fraction $\frac{\rho^F}{\rho^S}$.

Let us return to the problem of deviations from equlibrium. By means of the definition (A.9) we can specify the assumption that these deviations are small:

1. All constitutive quantities appearing in field equations must be at most linear functions of the constitutive variables $\mathbf{G}, \acute{\mathbf{X}}^F, \Delta$.
2. The dissipation D may contain at most quadratic contributions of the constitutive variables $\mathbf{G}, \acute{\mathbf{X}}^F, \Delta$. Partial energies, and entropies do not depend on $\mathbf{G}$, and $\acute{\mathbf{X}}^F$ but they may contain a quadratic contribution of Δ. This exception is related to the structure of dissipation due to the relaxation of porosity.

We use also the assumption that the system is isotropic.

Inspection of the dissipation inequality shows immediately that under these assumptions both $\hat{n}$, and Λ^n must be linear homogeneous functions of Δ, i.e.

$$\hat{n} = -\frac{\Delta}{\tau}, \quad \Lambda^n = \Lambda_1^n \Delta, \quad \tau = \tau\left(\mathcal{C}_E\right), \quad \Lambda_1^n = \Lambda_1^n\left(\mathcal{C}_E\right), \tag{A.13}$$

The form of these relations has been chosen for convenience in the further analysis. Simultaneously due to relations (A.5) we obtain

$$\mathbf{\Lambda}^{v^S} = \mathbf{\Lambda}^{v^F} = 0. \tag{A.14}$$

Bearing relations $(\text{A.5})_4$ $(\text{A.13})_2$ in mind we see that the contribution of Δ to energies, and entropies must be quadratic, and such that multipliers Λ^S, Λ^F, and Λ^ε are independent of Δ.

The above assumption yields as well the following representations for vector fluxes

$$\begin{aligned}
&\mathbf{Q}^S + \mathbf{Q}^F = -K_\Theta\left(\mathcal{C}_E\right)\mathbf{G} + K_v\left(\mathcal{C}_E\right)\acute{\mathbf{X}}^F, \\
&\mathbf{J} = \Phi_\Theta\left(\mathcal{C}_E\right)\mathbf{G} + \Phi_v\left(\mathcal{C}_E\right)\acute{\mathbf{X}}^F, \\
&\mathbf{H}^S + \mathbf{H}^F = -H_\Theta\left(\mathcal{C}_E\right)\mathbf{G} + H_v\left(\mathcal{C}_E\right)\acute{\mathbf{X}}^F.
\end{aligned} \tag{A.15}$$

Substitution of these relations in (A.6) yields the following set of identities

$$1. \qquad \rho^F\left(\frac{\partial\eta^F}{\partial\rho^S} - \Lambda^\varepsilon\frac{\partial\varepsilon^F}{\partial\rho^S}\right) = -\frac{\partial H_v}{\partial\rho^S} + \Lambda^\varepsilon\frac{\partial K_v}{\partial\rho^S} + \Lambda_1^n\Delta\frac{\partial\Phi_v}{\partial\rho^S},$$

$$-\frac{\partial H_\Theta}{\partial\rho^S} + \Lambda^\varepsilon\frac{\partial K_\Theta}{\partial\rho^S} - \Lambda_1^n\Delta\frac{\partial\Phi_\Theta}{\partial\rho^S} = 0, \tag{A.16$_1$}$$

$$2. \qquad -\rho^S\left(\frac{\partial\eta^S}{\partial\rho^F} - \Lambda^\varepsilon\frac{\partial\varepsilon^S}{\partial\rho^F}\right) = -\frac{\partial H_v}{\partial\rho^F} + \Lambda^\varepsilon\frac{\partial K_v}{\partial\rho^F} + \Lambda_1^n\Delta\frac{\partial\Phi_v}{\partial\rho^F},$$

$$-\frac{\partial H_\Theta}{\partial\rho^F} + \Lambda^\varepsilon\frac{\partial K_\Theta}{\partial\rho^F} - \Lambda_1^n\Delta\frac{\partial\Phi_\Theta}{\partial\rho^F} = 0, \tag{A.16$_2$}$$

$$3. \qquad \overset{23}{\operatorname{sym}}\left\{\rho^F\left(\frac{\partial\eta^F}{\partial\mathbf{F}^S} - \Lambda^\varepsilon\frac{\partial\varepsilon^F}{\partial\mathbf{F}^S} + \Lambda^F\mathbf{F}^{S-T}\right) - \left(H_v - \Lambda^\varepsilon K_v - \Lambda_1^n\Delta\Phi_v\right)\mathbf{F}^{S-T} + \right.$$

$$\left. + \left(\frac{\partial H_v}{\partial\mathbf{F}^S} - \Lambda^\varepsilon\frac{\partial K_v}{\partial\mathbf{F}^S} - \Lambda_1^n\Delta\frac{\partial\Phi_v}{\partial\mathbf{F}^S}\right)\right\} \otimes \acute{\mathbf{X}}^F + \tag{A.16$_3$}$$

$$+\overset{23}{\operatorname{sym}}\left\{-\frac{\partial H_\Theta}{\partial\mathbf{F}^S} + \Lambda^\varepsilon\frac{\partial K_\Theta}{\partial\mathbf{F}^S} - \Lambda_1^n\Delta\frac{\partial\Phi_\Theta}{\partial\mathbf{F}^S}\right\} \otimes \mathbf{G} = 0\ ,$$

$$4. \qquad -H_\Theta + \Lambda^\varepsilon K_\Theta - \Lambda_1^n\Delta\Phi_\Theta = 0; \tag{A.16$_4$}$$

with the relation containing derivatives with respect to n of thermal components of fluxes identically satisfied. According to the above assumption we account only for the first order contributions with respect to $\acute{\mathbf{X}}^F$, $\mathbf{G}$, and Δ. This concerns also identities following from (A.16$_3$) after simplifying with respect to $\acute{\mathbf{X}}^F$, and $\mathbf{G}$.

The relations for stresses become now true constitutive relations

$$\begin{aligned}
\Lambda^\varepsilon \mathbf{P}^S &= -\boldsymbol{\Lambda}^F - \left(\rho^F \Lambda^F - H_v + \Lambda^\varepsilon K_v + \Delta\Lambda_1^n \Phi_v\right)\mathbf{F}^{S-T}, \\
\Lambda^\varepsilon \mathbf{P}^F &= \left(\rho^F \Lambda^F - H_v + \Lambda^\varepsilon K_v + \Delta\Lambda_1^n \Phi_v\right)\mathbf{F}^{S-T},
\end{aligned} \tag{A.17}$$

and the residual inequality has the form

$$\begin{aligned}
&\left[\rho^F\left(\frac{\partial \eta^F}{\partial \Theta} - \Lambda^\varepsilon \frac{\partial \varepsilon^F}{\partial \Theta}\right) + \left(\frac{\partial H_v}{\partial \Theta} - \Lambda^\varepsilon \frac{\partial K_v}{\partial \Theta} - \Lambda_1^n \Delta \frac{\partial \Phi_v}{\partial \Theta}\right)\right]\acute{\mathbf{X}}^F \cdot \mathbf{G} - \\
&-\left(\frac{\partial H_\Theta}{\partial \Theta} - \Lambda^\varepsilon \frac{\partial K_\Theta}{\partial \Theta} + \Lambda_1^n \Delta \frac{\partial \Phi_\Theta}{\partial \Theta}\right)\mathbf{G}\cdot\mathbf{G} + \Lambda^\varepsilon\left(\hat{\mathbf{p}}^S - \hat{\rho}^S \acute{\mathbf{x}}^S\right)\cdot\left(\acute{\mathbf{x}}^F - \acute{\mathbf{x}}^S\right) \\
&-\frac{1}{\tau}\Lambda_1^n \Delta^2 + \hat{\rho}^S\left[\left(\eta^S + \Lambda^S - \Lambda^\varepsilon \varepsilon^S\right) - \left(\eta^F + \Lambda^F - \Lambda^\varepsilon \varepsilon^F\right) - \right. \\
&\left. -\frac{1}{2}\Lambda^\varepsilon\left(\acute{\mathbf{x}}^F - \acute{\mathbf{x}}^S\right)\cdot\left(\acute{\mathbf{x}}^F - \acute{\mathbf{x}}^S\right)\right] \geq 0.
\end{aligned} \tag{A.18}$$

It is clear that the approximation made above cannot admit mixed terms of this form as the first contribution to the above inequality. Hence we have in addition

$$\rho^F\left(\frac{\partial \eta^F}{\partial \Theta} - \Lambda^\varepsilon \frac{\partial \varepsilon^F}{\partial \Theta}\right) + \left(\frac{\partial H_v}{\partial \Theta} - \Lambda^\varepsilon \frac{\partial K_v}{\partial \Theta} - \Lambda_1^n \Delta \frac{\partial \Phi_v}{\partial \Theta}\right) = 0. \tag{A.19}$$

The relation (A.16$_4$) indicates that $\Phi_\Theta = 0$. The same relation together with (A.16$_{1,2,3}$) yields that Λ^ε depends solely on the temperature Θ. Then the classical argument for the state of equilibrium gives

$$\Lambda^\varepsilon = \frac{1}{\Theta}. \tag{A.20}$$

The structure of the multiplier Λ^n given by (A.13) indicates that the partial energies and entropies may contain solely terms independent of Δ or quadratic in Δ.

Now it is convenient to introduce the following notation

$$\psi^F = \varepsilon^F - \Theta\eta^F, \quad \psi^S = \varepsilon^S - \Theta\eta^S, \tag{A.21}$$

ψ^F, and ψ^S are, of course, the prototypes of Helmholtz free energies. These are constitutive quantities as well. We substitute them in the above relations after presenting another simplification.

Namely it is easy to show that it is compatible with the above thermodynamical structure to require the following condition to hold

$$H_v = \frac{1}{\Theta} K_v. \tag{A.22}$$

Then

$$\frac{\partial \psi^S}{\partial \rho^F} = 0,$$

$$\frac{\partial \psi^F}{\partial \rho^S} = 0, \quad \frac{\partial \psi^F}{\partial \mathbf{F}^S} = -\rho^F \frac{\partial \psi^F}{\partial \rho^F} \mathbf{F}^{S-T},$$

$$\frac{\partial \Phi_v}{\partial \rho^S} = 0, \quad \frac{\partial \Phi_v}{\partial \rho^F} = 0, \quad \frac{\partial \Phi_v}{\partial \mathbf{F}^S} = \Phi_v \mathbf{F}^{S-T}, \quad \frac{\partial \Phi_v}{\partial \Theta} = 0,$$

i.e.[2]

$$\begin{aligned} \psi^F &= \psi^F\left(\rho^F J^{S-1}, \Theta, \Delta\right), \quad \psi^S = \psi^S\left(\rho^S, \mathbf{F}^S, \Theta, \Delta\right), \\ \Phi_v &= \varphi J^S, \quad \varphi = const, \end{aligned} \tag{A.23}$$

and

$$K_v = \Theta \rho^F \left(\frac{\partial \psi^F}{\partial \Theta} + \eta^F \right). \tag{A.24}$$

In thermodynamics of single component materials the right hand side of this relation is identically zero. It may also be the case in the present model but the second law of thermodynamics does not impose this condition.

Let us summarize the results. Apart from the constitutive relations (A.23) for free energies which should be in addition quadratic with respect to Δ we have

$$\mathbf{Q}^S + \mathbf{Q}^F = \Theta\left(\mathbf{H}^S + \mathbf{H}^F\right) = -K_\Theta \mathbf{G} + K_v \acute{\mathbf{X}}^F, \tag{A.25}$$

with K_v given by (A.24). Simultaneously

$$\mathbf{J} = \varphi J^S \acute{\mathbf{X}}^F, \quad \varphi = const. \tag{A.26}$$

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[2] The analogous result has been obtained for isothermal conditions in my earlier works (e.g.[3]) under the assumption of constant equilibrium porosity n_E. This assumption is not made in this work, and, consequently, the result for φ should be understood as a dependence on an initial value of the equilibrium porosity. This is a consequence of the assumption that processes deviate little from the thermodynamical equilibrium

Partial stresses are given by the relations

$$\begin{aligned}
\mathbf{P}^S &= \rho^S \frac{\partial \psi^S}{\partial \mathbf{F}^S} - \Theta \Lambda_1^n \varphi J^S \Delta \mathbf{F}^{S-T}, \\
\mathbf{P}^F &= \left(-p^F + \Theta \Lambda_1^n \varphi \Delta\right) J^S \mathbf{F}^{S-T}, \quad p^F := \rho^{F2} \frac{\partial \psi^F}{\partial \rho^F} J^{S-1},
\end{aligned} \tag{A.27}$$

$$\Lambda_1^n = -\frac{1}{\Theta}\left(\rho^S \frac{\partial \psi^S}{\partial \Delta} + \rho^F \frac{\partial \psi^F}{\partial \Delta}\right). \tag{A.28}$$

The residual inequality defining the dissipation has the form

$$\begin{aligned}
&\frac{1}{\Theta} K_\Theta \mathbf{G} \cdot \mathbf{G} + \left(\hat{\mathbf{p}}^S - \hat{\rho}^S \acute{\mathbf{x}}^S\right) \cdot \left(\acute{\mathbf{x}}^F - \acute{\mathbf{x}}^S\right) + \left(\rho^S \frac{\partial \psi^S}{\partial \Delta} + \rho^F \frac{\partial \psi^F}{\partial \Delta}\right) \frac{1}{\tau} \Delta^2 + \\
&+ \hat{\rho}^S \left(\psi^F + \frac{p^F}{\rho^F J^{S-1}} - \psi^S - \rho^S \frac{\partial \psi^S}{\partial \rho^S}\right) \geq 0,
\end{aligned} \tag{A.29}$$

where due to the assumption on small deviations from equilibrium the quadratic contribution of the relative velocity to the mass source was neglected.

As usual in linear nonequilibrium thermodynamics we assume sources to be proportional to their conjucated forces, and, consequently, due to the isotropy we have

$$\begin{aligned}
&\left(\hat{\mathbf{p}}^S - \hat{\rho}^S \acute{\mathbf{x}}^S\right) = \pi \left(\acute{\mathbf{x}}^F - \acute{\mathbf{x}}^S\right), \\
&\hat{\rho}^S = R \left(\psi^F + \frac{p^F}{\rho^F J^{S-1}} - \psi^S - \rho^S \frac{\partial \psi^S}{\partial \rho^S}\right),
\end{aligned} \tag{A.30}$$

where π, and R are phenomenological coefficients.

This completes considerations of the local thermodynamical admissibility.

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