Nonisothermal immiscible compressible thermodynamically consistent two-phase flow in porous media

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A R T I C L E   I N F O

A B S T R A C T

In this paper, we introduce a new model of the nonisothermal immiscible compressible thermodynamically consistent two-phase flow in a porous domain Ω. This model includes the term describing the skeleton and interphase boundary energies. In the framework of the model, we derive the equation for the entropy function in the whole Ω and then obtain the estimate of the maximal entropy of the system.

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1. Introduction

In this paper, we study a model of nonisothermal immiscible compressible thermodynamically consistent two-phase flow in a porous reservoir Ω. The goal of the paper is to introduce the equations of the model and to derive the equation for the entropy function in the whole Ω and then obtain the estimate of the maximal entropy of the system.

It is important to notice that nowadays we observe an extensive literature on the various models of two-phase flow in porous media essentially more complicated than the classical models considered, e.g., in [1,2]. We will not attempt a literature review here, but merely mention a few references concerning the multicomponent compositional two-phase models, the reactive two-phase flow, the non-local two-phase flow etc. (see, e.g., [3–7] and the references therein). In this paper, for the sake of simplicity, we consider only the case of two homogeneous phases without interphase mass exchange. More complicated models, such as multicomponent compositional two-phase ones, can be rewritten in a thermodynamically consistent way by adding the surface energy, as shown in the paper. Further, the treatment of a reactive flow, added to the complexity of the model and an extension of our results to reactive models, although not straightforward, would be also possible. Relating the energy of the phase boundaries and the capillary pressure (1) can also be used in these more complex cases to obtain thermodynamically consistent models. However, this work is out of the scope of the paper.

In the case of inhomogeneous reservoirs when the flow process under the impact of the capillary pressure gradient plays a dominant role, the contribution of surface energy to the total energy balance can be significant. This leads us to the conclusion that the choice of a thermodynamically consistent flow model is preferable. The thermodynamically consistent models of nonisothermal flow take into account the surface energy of the interfaces between the fluid phases (in the first

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and second laws of the thermodynamics), i.e. in the energy balance, as well as in deriving the relations that guarantee the non-negativity of dissipation in arbitrary processes (see, e.g., [8–13]). The locally equilibrium models correspond to a slow (quasi-static, with a certain sign of change in saturation in order to eliminate the hysteresis phenomena of equilibrium capillary pressure curves) evolution of the system parameters. The dissipation of capillary forces in such processes is assumed to be zero. This leads to the relation between the energy of the phase boundaries E_{int} and the capillary pressure P_c. It reads:

$$P_c(S_w) = p_n - p_w = -\frac{\partial E_{int}}{\partial S_w} \tag{1}$$

where p_n, p_w stand for the pressures of the nonwetting and wetting phases, and S_w is the saturation of the wetting phase.

From the mathematical point of view, the results of the paper enable to carry out a rigorous mathematical analysis (including the homogenization process) of the equations describing the nonisothermal compressible flow in porous media with a nondeformable skeleton. An example of such analysis is given in [14,15], where a model of nonisothermal flow of two immiscible incompressible liquids was considered and the existence of a weak solution in the corresponding functional space was shown in the framework of the phase formulation under some realistic assumptions. However, these works do not take into account the compressibility of the fluids, and the energy equation does not involve the surface energy of the interfaces between the phases, which makes the model thermodynamically inconsistent. Both of these assumptions will imply some additional conditions that are necessary to study such kind of models.

Thus, in this paper, we formulate a thermodynamically consistent two-phase non-isothermal flow model with the defining relation (1), which assumes the local capillary equilibrium. Then, based on some realistic assumptions, we obtain the estimate of the maximal entropy of the system.

The rest of the paper is organized as follows. In Section 2, we introduce the main physical quantities involved in the model of a nonisothermal immiscible compressible thermodynamically consistent two-phase flow in porous media and formulate the assumptions on these quantities. Then, in Section 3, we present the governing equations of the model. Section 4 is devoted to the derivation of the entropy balance equation. Then using the results of the previous sections, we obtain the estimate of the maximal entropy. This is done in Section 5. Finally, the paper is completed by the concluding remarks, where we discuss briefly the aspects of the rigorous mathematical analysis of the nonisothermal immiscible compressible thermodynamically consistent two-phase flow model given in Section 3.

2. The physical quantities and main assumptions

The goal of the section is to define the main physical quantities that appear below in the model of the nonisothermal immiscible compressible thermodynamically consistent two-phase flow in porous media and to give the corresponding notation. In this paper, we follow mainly the definitions given in [16]. We have:

– *the time interval of interest:* it is $(0, \mathcal{T})$;
– *the domain of interest:* it is denoted by Ω;
– *the temperature:* $T = T(x, t)$ stands for the temperature in Ω. In this paper, we assume that the temperature is in a locally heat equilibrium state, i.e.

$$T_w = T_n = T_s = T$$

where, from now on, the indexes w, n, s correspond to the wetting, nonwetting phases, and the skeleton. In addition, we also assume that

$$T > 0 \quad \text{in the cylinder } \mathcal{Q} = \Omega \times (0, \mathcal{T}) \tag{2}$$

– *the phase pressures:* we denote by $p_w = p_w(x, t)$, $p_n = p_n(x, t)$ the pressures of the wetting and nonwetting fluids in Ω;
– *the phase density functions:* we denote by $\varrho_w(T, p_w)$, $\varrho_n(T, p_n)$ the true densities of wetting and nonwetting fluids, respectively;
– *the densities of the phase energies:* we denote by $E_w(T, p_w)$, $E_n(T, p_n)$ the true densities of energy of the wetting and nonwetting fluids, respectively;
– *the chemical potential:* we denote By ϕ_w, ϕ_n the chemical phase potentials of the wetting and nonwetting fluids, respectively;
– *the densities of the phase entropies:* for the introduced thermodynamic functions, we assume that the thermodynamic consistency conditions hold. These conditions imply the possibility to introduce the phase entropies with the densities $H_w(T, p_w)$, $H_n(T, p_n)$ by the following relations:

$$T \, dH_w = dE_w - \phi_w \, d\varrho_w \quad \text{and} \quad T \, dH_n = dE_n - \phi_n \, d\varrho_n \tag{3}$$

From now on, the differential d stands either for the partial derivative with respect to the time variable t or with respect to the space variable x_i. The thermodynamic phase stability conditions will be formulated below.

– *The saturation functions.* We denote by $S_w = S_w(x, t)$ and $S_n = S_n(x, t)$ the saturations of the wetting and nonwetting fluids in the domain Ω, respectively. Moreover,

$$S_w, S_n \geqslant 0 \quad \text{and} \quad S_w + S_n = 1 \tag{4}$$

– *The capillary pressure.* The capillary pressure function P_c is given by:

$$P_c(S_w) = p_n - p_w \tag{5}$$

We assume that the capillary pressure function is a smooth decreasing function of the wetting fluid saturation, i.e.

$$P'_c(S_w) < 0 \quad \text{for } S_w \in [0, 1] \tag{6}$$

– *The skeleton and interfacial boundary energies.* By E_{int} we denote the densities of the energy of the interfacial boundary per unit volume of the pore space (see, e.g., [8]). We assume that this energy depends on the phase saturations (as an independent variable, we take S_w) and the local properties of the skeleton, i.e. $E_{int} = E_{int}(S_w, x)$. In the framework of this assumption, the interfacial boundary entropy equals zero. The capillary pressure function is then related to the interfacial boundary energy by:

$$P_c(S_w) = -\frac{\partial E_{int}}{\partial S_w} \tag{7}$$

It follows from (5), (7) that (up to a constant) the energy of the interior boundaries is given by:

$$E_{int} = \int_{S_w}^{1} P_c(\xi) \, d\xi \tag{8}$$

– *The viscosity function.* By $\mu_w = \mu_w(T)$, $\mu_n = \mu_n(T)$ we denote the viscosities of wetting and nonwetting fluids in Ω.
– *Assumption on the skeleton.* We assume that the skeleton is incompressible, i.e. the skeleton phase density ϱ_s is a constant and its true energy density depends on the temperature, only. Namely, $E_s = E_s(T)$. The skeleton entropy density $H_s = H_s(T)$ is given by:

$$dE_s = T \, dH_s \tag{9}$$

– *The porosity function.* We denote by Φ the porosity of the domain Ω. The porosity Φ is a constant such that $0 < \Phi < 1$.
– *The absolute permeability function.* We denote by K the constant absolute permeability of the domain Ω such that $0 < K < +\infty$.
– *The relative permeability functions.* We denote by $k_{r,w} = k_{r,w}(S_w)$ and $k_{r,g} = k_{r,g}(S_n)$ the relative permeabilities of the wetting and nonwetting fluids in Ω. We assume that $k_{r,w}$, $k_{r,g}$ are continuous functions and satisfy the following properties: **(i)** $0 \leqslant k_{r,w}, k_{r,g} \leqslant 1$ on $\mathbb{R}$; **(ii)** $k_{r,w}(S) = 0$ for $S \leqslant 0$ and $k_{r,g}(S) = 0$ for $S \geqslant 1$; $k_{r,w}(S) = 1$ for $S \geqslant 1$ and $k_{r,g}(S) = 1$ for $S \leqslant 0$; **(iii)** there is a positive constant k_0 such that $k_{r,w}(S) + k_{r,g}(S) \geqslant k_0 > 0$ for all $S \in \mathbb{R}$.
– *The mobility functions.* The mobility functions $\lambda_w(S_w, T)$ and $\lambda_n(S_w, T)$ are defined by:

$$\lambda_w(S_w, T) = \frac{k_{r,w}(S_w)}{\mu_w(T)} \quad \text{and} \quad \lambda_n(S_n, T) = \frac{k_{r,g}(S_n)}{\mu_n(T)} \tag{10}$$

– *The Darcy velocities.* The velocities of the wetting and nonwetting fluids $\mathbf{q}_w$, $\mathbf{q}_n$ are defined by the Darcy–Muskat law:

$$\mathbf{q}_w = -K \, \lambda_w(S_w, T) \, \nabla p_w \quad \text{and} \quad \mathbf{q}_n = -K \, \lambda_n(S_n, T) \, \nabla p_n \tag{11}$$

– *The effective thermal conductivity.* By k_T we denote the constant effective thermal conductivity. In addition, we define:

$$\mathbf{q}_T = -k_T \, \nabla T \tag{12}$$

Remark 1. In this paper, for the sake of simplicity and brevity, we assume that the functions P_c, E_{int}, Φ, K, and k_T do not depend on the space variable x.

Remark 2. It is necessary to notice that the assumption (2) on the temperature function T is rather restrictive and is possibly not true. In order to overcome this difficulty, we can impose an additional condition on the viscosities μ_w, μ_n assuming that the functions $\mu_w = \mu_w(T)$, $\mu_n = \mu_n(T)$ go to infinity as the temperature function T goes to zero. In this case, the mobility functions $\lambda_w(S_w, T)$, $\lambda_n(S_w, T)$ become zero. Thus the system of the governing equations presented in (13) are valid for $T > 0$, only.

3. The governing equations of the model

In this section we introduce the physical-mathematical model which will be studied in the paper. We consider a non-isothermal immiscible compressible two-phase flow process in a porous domain $\Omega \subset \mathbb{R}^d$ $(d = 1, 2, 3)$ which is assumed to be a bounded domain. The conservation of mass in each phase and conservation of energy can be written as:

$$
\begin{cases}
\Phi \dfrac{\partial}{\partial t}[S_w \varrho_w] + \operatorname{div}\{\varrho_w \mathbf{q}_w\} = 0 \quad \text{in } \mathcal{Q} \\[2mm]
\Phi \dfrac{\partial}{\partial t}[S_n \varrho_n] + \operatorname{div}\{\varrho_n \mathbf{q}_n\} = 0 \text{ in } \mathcal{Q} \\[2mm]
\dfrac{\partial}{\partial t}\Big[\Phi E_f + (1 - \Phi) E_s\Big] + \\[2mm]
\qquad + \operatorname{div}\Big\{(E_w + p_w)\,\mathbf{q}_w + (E_n + p_n)\,\mathbf{q}_n + \mathbf{q}_T\Big\} = 0 \quad \text{in } \mathcal{Q} \\[2mm]
P_c(S_w) = p_n - p_w \quad \text{in } \mathcal{Q}
\end{cases}
\tag{13}
$$

where $\mathcal{Q} = \Omega \times (0, \mathcal{T})$, the basic physical quantities are described in Section 2, and where

$$
E_f = E_w S_w + E_n S_n + E_{\text{int}}(S_w, x)
\tag{14}
$$

System (13) has to be completed by the corresponding boundary and initial conditions.

Boundary conditions on the external boundary. We impose the Neumann boundary conditions on the internal boundary $\partial \Omega$:

$$
\begin{cases}
\mathbf{q}_w \cdot \mathbf{n} = \mathbf{q}_n \cdot \mathbf{n} = 0 & \text{on } \partial \Omega \times (0, \mathcal{T}) \\[2mm]
k_T \nabla T \cdot \mathbf{n} = 0 & \text{on } \partial \Omega \times (0, \mathcal{T})
\end{cases}
\tag{15}
$$

Initial conditions. The initial conditions read:

$$
p_w(x, 0) = p_w^0(x), \quad p_g(x, 0) = p_g^0(x), \quad T(x, 0) = T^0(x) \quad \text{in } \Omega
\tag{16}
$$

4. The entropy balance equation

Let us obtain the entropy balance equation for the two-phase nonisothermal flow in porous medium Ω. The main result of the section is as follows.

Proposition 4.1. *The entropy balance equation reads:*

$$
\Phi \frac{\partial}{\partial t}\Big(H_w S_w + H_n S_n\Big) + (1 - \Phi)\frac{\partial H_s}{\partial t} + \operatorname{div}\Big\{H_w \mathbf{q}_w + H_n \mathbf{q}_n + \frac{\mathbf{q}_T}{T}\Big\}
$$
$$
= K \frac{\lambda_w(S_w, T)|\nabla p_w|^2 + \lambda_n(S_n, T)|\nabla p_n|^2}{T} + \frac{k_T |\nabla T|^2}{T^2}
\tag{17}
$$

where H_w, H_n, and H_s are the entropy densities of the wetting, nonwetting fluids, and the skeleton.

Proof of Proposition 4.1. Let us multiply the fluid mass balance equations $(13)_1$ and $(13)_2$ by the phase chemical potentials ϕ_w and ϕ_n, respectively, and then take a sum. We get:

$$
\Phi \frac{\partial}{\partial t}\Big[\phi_w \varrho_w S_w + \phi_n \varrho_n S_n\Big] - \Phi\Big[\varrho_w S_w \frac{\partial \phi_w}{\partial t} + \varrho_n S_n \frac{\partial \phi_n}{\partial t}\Big] +
$$
$$
+ \operatorname{div}\Big\{\phi_w \varrho_w \mathbf{q}_w + \phi_n \varrho_n \mathbf{q}_n\Big\} - \Big\{\varrho_w \mathbf{q}_w \cdot \nabla \phi_w + \varrho_n \mathbf{q}_n \cdot \nabla \phi_n\Big\} = 0
\tag{18}
$$

Let us recall the Gibbs–Duhem formulae:

$$
H_w \, dT + \varrho_w \, d\phi_w = dp_w \quad \text{and} \quad H_n \, dT + \varrho_n \, d\phi_n = dp_n
\tag{19}
$$

Then, from (18) and (19), we have:

$$\Phi \frac{\partial}{\partial t}\Big(\phi_w \varrho_w S_w + \phi_n \varrho_n S_n\Big) - \Phi\Big(S_w \frac{\partial p_w}{\partial t} + S_n \frac{\partial p_n}{\partial t}\Big)$$
$$+ \Phi\Big(H_w S_w \frac{\partial T}{\partial t} + H_n S_n \frac{\partial T}{\partial t}\Big) + \mathrm{div}\Big\{\phi_w \varrho_w \mathbf{q}_w + \phi_n \varrho_n \mathbf{q}_n\Big\} \tag{20}$$
$$- \Big\{\mathbf{q}_w \cdot \nabla p_w + \mathbf{q}_n \cdot \nabla p_n\Big\} + \Big\{H_w \mathbf{q}_w \cdot \nabla T + H_n \mathbf{q}_n \cdot \nabla T\Big\} = 0$$

Now, we make use of the density of the Gibbs phase potentials, i.e.

$$\phi_w \varrho_w = E_w + p_w - T H_w \quad \text{and} \quad \phi_n \varrho_n = E_n + p_n - T H_n \tag{21}$$

Subtracting Eq. (20) from the energy balance Eq. (13)₃ and taking into account (21), we get:

$$\Phi T \frac{\partial}{\partial t}\Big(H_w S_w + H_n S_n\Big) + \Phi\left[\frac{\partial E_{\text{int}}}{\partial t} - \Big(p_w \frac{\partial S_w}{\partial t} + p_n \frac{\partial S_n}{\partial t}\Big)\right]$$
$$+ \big(1 - \Phi\big)\frac{\partial E_s}{\partial t} + \mathrm{div}\Big\{T H_w \mathbf{q}_w + T H_n \mathbf{q}_n + \mathbf{q}_T\Big\} - \tag{22}$$
$$+ \Big\{\mathbf{q}_w \cdot \nabla p_w + \mathbf{q}_n \cdot \nabla p_n\Big\} - \Big\{H_w \mathbf{q}_w \cdot \nabla T + H_n \mathbf{q}_n \cdot \nabla T\Big\}$$

By the definition:

$$E_{\text{int}} = -\int_0^{S_w} P_c(\xi)\,\mathrm{d}\xi \quad \text{with } P_c(S_w) = p_n - p_w \tag{23}$$

we have

$$\frac{\partial E_{\text{int}}}{\partial t} - \Big(p_w \frac{\partial S_w}{\partial t} + p_n \frac{\partial S_n}{\partial t}\Big) = 0$$

Then, taking into account that $\mathrm{d}E_s = T\,\mathrm{d}H_s$, Eq. (22) becomes:

$$\Phi T \frac{\partial}{\partial t}\Big(H_w S_w + H_n S_n\Big) + \big(1 - \Phi\big)T \frac{\partial H_s}{\partial t}$$
$$+ T\,\mathrm{div}\Big\{H_w \mathbf{q}_w + H_n \mathbf{q}_n + \frac{\mathbf{q}_T}{T}\Big\} \tag{24}$$
$$+ \mathbf{q}_w \cdot \nabla p_w + \mathbf{q}_n \cdot \nabla p_n + T \mathbf{q}_T \cdot \nabla \frac{1}{T} = 0$$

Dividing now Eq. (24) by the temperature and applying the definition of the phase velocities, we get the entropy balance, Eq. (17). Lemma 4.1 is proved. □

Now, as a consequence of Lemma 4.1, we obtain the equation for the entropy function in the whole Ω. To this end, we introduce the fluid entropy density:

$$H_f = S_w H_w + S_n H_n \tag{25}$$

where H_w, H_n are the true phase entropy densities. The entropy density (with respect to the whole volume) is then defined by:

$$H = \Phi H_f + \big(1 - \Phi\big) H_s \tag{26}$$

Then we introduce the entire entropy function:

$$\mathcal{H} = \int_\Omega H\,\mathrm{d}x \tag{27}$$

Now from (17) and (25)-(26) we get the following relation:

$$\frac{\partial H}{\partial t} + \mathrm{div}\Big\{H_w \mathbf{q}_w + H_n \mathbf{q}_n + \frac{\mathbf{q}_T}{T}\Big\}$$
$$= K \frac{\lambda_w(S_w, T)|\nabla p_w|^2 + \lambda_n(S_n, T)|\nabla p_n|^2}{T} + k_T \frac{|\nabla T|^2}{T^2} \tag{28}$$

Let us integrate (28) over Ω. Then taking into account the boundary conditions (15), we get:

$$\frac{d\mathcal{H}}{dt} = \int_{\Omega} \left[K \frac{\lambda_w(S_w, T)|\nabla p_w|^2 + \lambda_n(S_n, T)|\nabla p_n|^2}{T} + k_T \frac{|\nabla T|^2}{T^2} \right] dx \tag{29}$$

5. The estimate of the maximal entropy

Let us recall that the density of the fluid energy E_f is defined by (14). In this definition, E_{int}, the energy of the interphase density, depends, generally speaking, on the local domain properties. In what follows, the coordinate dependence of E_{int} is assumed to be parametric. We also recall that the fluid entropy density is given by (25). In addition, in the model considered in this paper, the entropy of the interphase boundaries is equal to zero, since the energy density of the interphase boundaries does not depend on the temperature. Then the differentials of the corresponding densities have the form:

$$dE_f = S_w dE_w + S_n dE_n + (E_w - E_n) dS_w + dE_{int} \tag{30}$$

$$dH_f = S_w dH_w + S_n dH_n + (H_w - H_n) dS_w \tag{31}$$

Now taking into account the thermodynamical relations:

$$dE_w = T dH_w + \phi_w d\varrho_w \quad \text{and} \quad dE_n = T dH_n + \phi_n d\varrho_n \tag{32}$$

one obtains that

$$\begin{aligned} dE_f = {}& (T dH_w + \phi_w d\varrho_w) S_w \\ & + (T dH_n + \phi_n d\varrho_n) S_n + (E_w dS_w + E_n dS_n) + dE_s \end{aligned} \tag{33}$$

Equation (33) can be rewritten as follows:

$$\begin{aligned} dE_f - T dH_f = {}& S_w \phi_w d\varrho_w + S_n \phi_n d\varrho_n \\ & + (E_w - T dH_w) dS_w + (E_n - T dH_n) dS_n + dE_{int} \end{aligned} \tag{34}$$

where we recall that ϱ_w, ϱ_n stand for the true phase densities and ϕ_w, ϕ_n are the chemical phase potentials.

Let us introduce the effective phase densities in the porous space. They are defined as follows:

$$\theta_w = \varrho_w S_w \quad \text{and} \quad \theta_n = \varrho_n S_n \tag{35}$$

Then

$$d\theta_w = \varrho_w dS_w + S_w d\varrho_w \quad \text{and} \quad \theta_n = \varrho_n dS_n + S_n d\varrho_n \tag{36}$$

Plugging (36) in (34), we get:

$$\begin{aligned} dE_f - T dH_f &= \phi_w \left[d(\varrho_w S_w) - \varrho_w dS_w \right] + \phi_n \left[d(S_n \varrho_n) - \varrho_n dS_n \right] \\ & \quad + (E_w - TH_w) dS_w + (E_n - TH_n) dS_n + dE_{int} \\ &= \phi_w d\theta_w + \phi_n d\theta_n + (E_w - TH_w - \phi_w \varrho_w) dS_w \\ & \quad + (E_n - TH_n - \phi_n \varrho_n) dS_n + dE_{int} \\ &= \phi_w d\theta_1 + \phi_n d\theta_2 + (p_n - p_w) dS_w + dE_{int} \end{aligned} \tag{37}$$

The condition of the interphase equilibrium reads (see (1)):

$$p_n - p_w = P_c(S_w) = -\frac{\partial E_{int}}{\partial S_w} \tag{38}$$

Finally, we obtain that

$$dE_f = T dH_f + \phi_w d\theta_w + \phi_n d\theta_n$$

This leads to the following equality:

$$dH_f = \frac{dE_f}{T} - \frac{\phi_w d\theta_w}{T} - \frac{\phi_n d\theta_n}{T} \tag{39}$$

Taking into account the skeleton phase, the energy and entropy (with respect to the whole volume) densities become:

$$E = \Phi E_f + (1 - \Phi) E_s \tag{40}$$

$$H = \Phi H_{\mathrm{f}} + \left(1 - \Phi\right) H_{\mathrm{s}} \tag{41}$$

These definitions imply that

$$\mathrm{d}E = \Phi \, \mathrm{d}E_{\mathrm{f}} + \left(1 - \Phi\right) \mathrm{d}E_{\mathrm{s}} \tag{42}$$

$$\mathrm{d}H = \Phi \, \mathrm{d}H_{\mathrm{f}} + \left(1 - \Phi\right) \mathrm{d}H_{\mathrm{s}} \tag{43}$$

Then taking into account (34)-(43), we obtain that

$$\mathrm{d}H = -\Phi \left[\frac{\phi_{\mathrm{w}} \, \mathrm{d}\theta_{\mathrm{w}}}{T} - \frac{\phi_{\mathrm{n}} \, \mathrm{d}\theta_{\mathrm{n}}}{T} \right] + \frac{\mathrm{d}E}{T}$$

In terms of (45), the differential $\mathrm{d}H$ can be rewritten as:

$$\mathrm{d}H = -\frac{\phi_{\mathrm{w}} \, \mathrm{d}m_{\mathrm{w}}}{T} - \frac{\phi_{\mathrm{n}} \, \mathrm{d}m_{\mathrm{w}}}{T} + \frac{\mathrm{d}E}{T} \tag{44}$$

Here m_{w}, m_{n} are effective phase densities defined by:

$$m_{\mathrm{w}} = \Phi \, \theta_{\mathrm{w}} \quad \text{and} \quad m_{\mathrm{n}} = \Phi \, \theta_{\mathrm{n}} \tag{45}$$

Relation (44) means that the entropy density of the triphasic system, i.e. two fluids and the skeleton, is a function of the effective fluid phase densities m_{w}, m_{n}, and the energy density E, which is equal to the sum of the phase energies and the energy of the interphase boundaries per volume unit of the space.

Notational convention. For the sake of brevity, we make use of the following notation:

$$U = \langle m_{\mathrm{w}}, m_{\mathrm{n}}, E \rangle = \langle u_1, u_2, u_3 \rangle$$

Now we are in position to discuss *the maximal system entropy* of our model. Due to the thermodynamical principles, in the case of the fixed volume, composition (the phase masses), and the energy, in the equilibrium state the entropy maximum is achieved. In the equilibrium state, the temperature and the chemical phase potentials do not depend on the coordinates. The mechanical equilibrium conditions are, in fact, the homogeneity of the phase pressures in space. The distributions of the true phase densities are also homogeneous. Moreover, the saturation distribution, the effective phase densities distribution are also homogeneous.

Proposition 5.1. *The maximal entropy is achieved in the case of the homogeneous distribution of the quantities T, ϕ_{w}, ϕ_{n} (or T, p_{w}, p_{n}) in space.*

Proof of Proposition 5.1. At the initial time moment $t = 0$, we have some distributions of the phase saturations, phase pressures, and the temperature (see (16)) above. Then we also have the distributions of the mass densities, the energy phase densities, and the interphase energy density. The phase masses and the energy of the system can be calculated by the basic physical quantities introduced in Section 2 by the following formulae:

$$\mathcal{M}_{\mathrm{w}} = \int_{\Omega} \Phi \, \varrho_{\mathrm{w}} \, S_{\mathrm{w}} \, \mathrm{d}x \quad \text{and} \quad \mathcal{M}_{\mathrm{n}} = \int_{\Omega} \Phi \, \varrho_{\mathrm{n}} \, S_{\mathrm{n}} \, \mathrm{d}x \tag{46}$$

$$\mathcal{E} = \mathcal{E}_{\mathrm{f}} + \mathcal{E}_{\mathrm{s}} = \int_{\Omega} \left\{ \left(S_{\mathrm{w}} E_{\mathrm{w}} + S_{\mathrm{n}} E_{\mathrm{n}} + E_{\mathrm{int}} \right) \Phi + \left(1 - \Phi\right) E_{\mathrm{s}} \right\} \mathrm{d}x \tag{47}$$

Notation convention. Let us denote the equilibrium effective phase densities, the energy density, and the equilibrium temperature by $\widehat{m}_{\mathrm{w}}(x)$, $\widehat{m}_{\mathrm{n}}(x)$, $\widehat{E}(x)$, and $\widehat{T}$, respectively.

Let us compare now the entropy in a non-equilibrium and the equilibrium states for the same phase masses and energy. The entropy density is a function of the effective phase mass densities and the energy density, i.e. $H = H(m_{\mathrm{w}}, m_{\mathrm{n}}, E)$. Then in the equilibrium state the entire entropy has the form:

$$\widehat{\mathcal{H}} = \int_{\Omega} H(\widehat{m}_{\mathrm{w}}, \widehat{m}_{\mathrm{n}}, \widehat{E}) \, \mathrm{d}x \tag{48}$$

and, consequently, in the non-equilibrium one, it reads:

$$\mathcal{H} = \int_{\Omega} H(m_{\mathrm{w}}, m_{\mathrm{n}}, E) \, \mathrm{d}x \tag{49}$$

Let us represent $H(m_w, m_n, E)$ by Taylor's formula in the neighborhood of the point $\widehat{U} = \langle \widehat{m}_w, \widehat{m}_n, \widehat{E} \rangle$. We have:

$$
\begin{aligned}
\mathcal{H} &= \widehat{\mathcal{H}} + \mathcal{R} \\
&\quad + \int_\Omega \left\{ \frac{\partial H}{\partial m_w}(\widehat{U})(m_w - \widehat{m}_w) + \frac{\partial H}{\partial m_n}(\widehat{U})(m_n - \widehat{m}_n) + \frac{\partial H}{\partial E}(\widehat{U})(E - \widehat{E}) \right\} dx \\
&= \widehat{\mathcal{H}} + \int_\Omega \left\{ \frac{\widehat{\phi}_w}{\widehat{T}}[m_w - \widehat{m}_w] + \frac{\widehat{\phi}_n}{\widehat{T}}[m_n - \widehat{m}_n] + \frac{1}{\widehat{T}}[E - \widehat{E}] \right\} dx + \mathcal{R} \\
&= \widehat{\mathcal{H}} + \frac{\widehat{\phi}_w}{\widehat{T}} \int_\Omega (m_w - \widehat{m}_w)\, dx + \frac{\widehat{\phi}_n}{\widehat{T}} \int_\Omega (m_n - \widehat{m}_n)\, dx + \frac{1}{\widehat{T}} \int_\Omega (E - \widehat{E})\, dx + \mathcal{R}
\end{aligned}
\tag{50}
$$

The integrals on the right-hand side of (50) equal zero due to the definition of the equilibrium phase mass densities, the energy density and the conservation of mass and energy law. The reminder term $\mathcal{R}$ is given by:

$$
\mathcal{R} = \frac{1}{2} \int_\Omega \sum_{i,j} \frac{\partial^2 H}{\partial u_i\, \partial u_j}(U^*)\,(u_i - \widehat{u}_i)(u_j - \widehat{u}_j)\, dx
\tag{51}
$$

where $U^* = \langle m_w^*(x), m_n^*(x), E^*(x) \rangle$ are some intermediate phase mass densities and the energy density, which depend on the coordinates and the time variable.

It is clear that if, in the variable scope of $\langle m_w, m_n, E \rangle$, the Jacobian $\mathcal{J}$ with the entries $\mathcal{J}_{ij} = \left\{ \frac{\partial^2 H}{\partial u_i\, \partial u_j} \right\}$ is such that $\sum_{i,j} \mathcal{J}_{ij} x_i x_j \leqslant 0$, then

$$
\mathcal{H} \leqslant \widehat{\mathcal{H}}
\tag{52}
$$

In other words, if the second differential

$$
d_{uu}^2 H = \frac{\partial^2 H}{\partial u_i\, \partial u_j}\, du_i du_j
$$

is nonnegative in the domain of definition of the variables $\langle m_w, m_n, E \rangle$, then the quantity $\widehat{\mathcal{H}}$ is an upper bound of the entropy in the domain Ω.

In order to prove this property of the second differential and find the conditions that guarantee this fact, along with the variables $\langle m_w, m_n, E \rangle$, we introduce the additional variables $V = \langle T, P, S_w \rangle$. These variables are assumed to be independent. Here P is a "mean" pressure defined by:

$$
P = S_w p_w + S_n p_n
\tag{53}
$$

The advantage of the pressure P with respect to the phases pressures is that it is defined even in the cases when one of the phase pressures equals zero. The variables $v_i = \langle T, P, S_w \rangle$ are more convenient for the calculations, and we assume that they are independent. It is known from the mathematical analysis that the second differential is not invariant to the change of variables. Let us consider the differential of the form:

$$
dH = \sum a_i du_i = -\frac{\phi_w\, dm_w}{T} - \frac{\phi_n\, dm_n}{T} + \frac{dE}{T}
\tag{54}
$$

Taking into account the fact that the variables $v_i = \langle T, P, S_w \rangle$ are independent, i.e. $d^2 T = d^2 P = d^2 S_w = 0$, we have that

$$
d_{vv}^2 H = d_{uu}^2 H + \sum a_i d^2 u_i
\tag{55}
$$

In order to calculate $d_{vv}^2 H$, we have to find the differential of

$$
T\, dH = dE - \phi_w\, dm_w - \phi_n\, dm_n
$$

Then we obtain that

$$
T\, d_{vv}^2 H + dT\, dH = d^2 E - \phi_w\, d^2 m_w - \phi_n\, d^2 m_n - d\phi_w\, dm_w - d\phi_n\, dm_n
\tag{56}
$$

Now one easily obtains that

$$
\begin{aligned}
T\, d_{uu}^2 H &= T\, d_{vv}^2 H - T \sum a_i d^2 u_i = T\, d_{vv}^2 H - \left(d^2 E - \phi_w\, d^2 m_w - \phi_n\, d^2 m_n \right) = \\
&= \left(d^2 E - \phi_w\, d^2 m_w - \phi_n\, d^2 m_n - d\phi_w\, dm_w - d\phi_n\, dm_n - dT\, dH \right) - \left(d^2 E - \phi_w\, d^2 m_w - \phi_n\, d^2 m_n \right)
\end{aligned}
$$

Finally, we get:

$$T \, d_{uu}^2 H = -dT \, dH - d\phi_w \, dm_w - d\phi_n \, dm_n \tag{57}$$

The definitions of the densities imply the following relations:

$$dH = \Phi \left[(H_w - H_n) \, dS_w + S_w \, dH_w + S_n \, dH_n \right] + (1 - \Phi) \, dH_s \tag{58}$$

$$dm_w = \Phi \left(S_w \, d\varrho_w + \varrho_w \, dS_w \right) \quad \text{and} \quad dm_n = \Phi \left(S_n \, d\varrho_n - \varrho_n \, dS_w \right) \tag{59}$$

Plugging (58), (59) in (57), we obtain that

$$
\begin{aligned}
T \, d_{uu}^2 H = &-\Phi \, dS_w \left[(H_w - H_n) \, dT + \varrho_w \, d\phi_w - \varrho_n \, d\phi_n \right] \\
&- \Phi \, S_w \left[dT \, dH_w + d\phi_w \, d\varrho_w \right] - \Phi \, S_n \left[dT \, dH_n + d\phi_n \, d\varrho_n \right] - (1 - \Phi) \, S_w \, dT \, dH
\end{aligned} \tag{60}
$$

Now we apply the Gibbs–Duhem formula, i.e.

$$dp_w = H_w \, dT + \rho_w \, d\phi_w \quad \text{and} \quad dp_n = H_n \, dT + \rho_n \, d\phi_n \tag{61}$$

Then we have:

$$
\begin{aligned}
T d_{uu}^2 H = &-\Phi \left[dp_w - dp_n \right] dS_w - S_w \left[dT \, dH_w + d\phi_w \, d\varrho_w \right] \\
&- S_n \left[dT \, dH_n + d\phi_n \, d\varrho_n \right] - (1 - \Phi) \, dT \, dH_s \\
= &\, \Phi \, P_c'(S_w) \, dS_w^2 - \Phi \, S_w \left[dT \, dH_w + d\phi_w \, d\varrho_w \right] \\
&- \Phi \, S_n \left[dT \, dH_n + d\phi_n \, d\varrho_n \right] - (1 - \Phi) \, dT \, dH_s
\end{aligned} \tag{62}
$$

Consider the first term on the right-hand side of (62). Let us recall that the capillary pressure function is assumed to satisfy conditions (5), (6). The last one, in particular, means the flow stability under the capillary forces. The nonnegativity of the forms

$$dT \, dH_w + d\phi_w \, d\varrho_w \quad \text{and} \quad dT \, dH_n + d\phi_n \, d\varrho_n$$

is the condition of the thermodynamical stability of the fluid phases, the nonnegativity of the form $dT \, dH_s$ is the condition of the thermodynamic stability of the skeleton phase.

Remark 3. One can easily verify these conditions, for example, in the case of an ideal gas and incompressible fluid. They are then reduced to the nonnegativity of the isochoric heat capacities and the isothermal compressibility coefficients along with the positivity of the temperature function. Namely, for the (ideal) gas, we have that $H_n = \varrho_n \eta_n$, where η_n is the specific entropy of the gas. Then $dH_n = \varrho_n \, d\eta_n + \eta_n \, d\varrho_n$. The differential of the chemical potential ϕ_n is given by $d\phi_n = -\eta_n \, dT + v_n \, dp_n$, where $v_n = 1/\varrho_n$ stands for the specific volume of the gas. We also have that

$$\frac{\partial \eta_n}{\partial p_n} = -\frac{\partial v_n}{\partial T} = -v_n \boldsymbol{\alpha}_T = \frac{\partial^2 \phi_n}{\partial p_n^2}$$

where $\boldsymbol{\alpha}_T$ is the thermal expansion coefficient. Then we have that

$$
\begin{aligned}
dT \, dH_n + d\phi_n \, d\varrho_n &= dT \left[\eta_n \, d\varrho_n + \varrho_n \, d\eta_n \right] + d\varrho_n \left[-\eta_n \, dT + v_n \, dp_n \right] = \\
&= \varrho_n \, dT \, d\eta_n + v_n \, d\varrho_n \, dp_n = \varrho_n \left[dT \, d\eta_n - dv_n \, dp_n \right]
\end{aligned} \tag{63}
$$

The differentials $d\eta_n$ and dv_n can be written as follows:

$$d\eta_n = \frac{c_{pg}}{T} \, dT + \frac{\partial \eta_n}{\partial p_n} \, dp_n = \frac{c_{pg}}{T} \, dT - \frac{\partial v_n}{\partial T} \, dp_n \quad \text{and} \quad dv_n = \frac{\partial v_n}{\partial p_n} \, dp_n + \frac{\partial v_n}{\partial T} \, dT \tag{64}$$

where c_{pg} is the isobaric heat capacity of the gas. Then it follows from (63), (64) that

$$dT \, dH_n + d\phi_n \, d\varrho_n = \varrho_n \left[\frac{c_{pg}}{T} \, dT^2 - 2 \frac{\partial v_n}{\partial T} \, dT \, dp_n - \frac{\partial v_n}{\partial p_n} \, dp_n^2 \right] \tag{65}$$

The conditions of positive semi-definiteness of the quadratic form (65) are:

$$\frac{\partial v_n}{\partial p_n} \leqslant 0 \quad \text{and} \quad -\frac{\partial v_n}{\partial p_n} \frac{c_{pg}}{T} - \left(\frac{\partial v_n}{\partial T} \right)^2 = -\frac{\partial v_n}{\partial p_n} \frac{c_{vg}}{T} \geqslant 0$$

where c_{vg} is the isochoric heat capacity of the gas. This gives the nonnegativity of the form $dT \, dH_n + d\phi_n \, d\varrho_n$.

Thus, if the fluid and skeleton phases are thermodynamically stable and the system is isolated (the volume, composition and the energy are constant), then the maximal entropy is achieved in the equilibrium state when the temperature and the phase pressures (or chemical potentials) are homogeneous and Proposition 5.1 is proved. □

6. Concluding remarks

In this paper, we have considered the nonisothermal immiscible compressible thermodynamically consistent two-phase flow in porous media in terms of the entropy function. It was done in a purely theoretical way. In the forthcoming paper, we will present the numerical simulation results for this model.

The work is done with an eye to the rigorous mathematical analysis of the nonisothermal compressible thermodynamically consistent two-phase flow in porous media. In the previous papers [14,15], the authors studied the existence and homogenization problems for the nonisothermal immiscible incompressible two-phase flow in porous media. The results obtained in this work enable us to generalize the results of [14] to the nonisothermal compressible two-phase flow in porous media. The key point in this study will be the proof of the maximum principle for the temperature function T, which remains an open question. This study will be the subject of forthcoming papers by us.

Acknowledgements

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