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A thermodynamic formulation for multiphase compositional flows in porous media

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Abstract

The main purpose of this work is to develop a practical and consistent model of multiphase flow in porous media. The thermodynamics of irreversible processes is applied to the representative elementary volume of a porous medium filled with multiple compositional fluids. The entropy production is derived and analyzed in order to establish phenomenological equations for the macroscopic fluxes and an equation of state for the matrix-fluids-interfaces system at equilibrium. The entropy dissipation due to the transformation of the interfaces is identified and its analysis gives a new model for capillarity with two phases or more. The physical model is formulated in a well-posed system of elliptic-parabolic differential equations based on a set of persistent primary variables. The formulation encompasses a wide range of classical models and extends them by handling an arbitrary number of phases and components.

Keywords: porous medium, multiphase flow, thermodynamics, capillarity, interface

1. Introduction

The idea that thermodynamics can help in building macroscopic descriptions of flows in porous media is explored since several decades [12, 18, 23, 24, 31, 33]. It led to significant insights, like interpreting the empirical Darcy's law [13] as the first order approximation of a dissipative process [31]. The purpose of thermodynamic approaches is to give theoretical foundations to the most used macroscopic equations and to develop accurate models for less known processes. One of their strengths is consistency, in opposition to a modelling strategy based on the analogy with phenomena in continuous medium and the superposition of the corresponding equations.

Although the thermodynamic approaches are multiple, they have in common to start with a thermodynamic description at the pore level, then to derive a macroscopic description from them. The approaches can differ at both steps. Concerning the transition from pore level to macroscopic level, the challenge is to properly relate the quantities and relations used at the two levels. The notion of a length scale separating between two levels of description appears independently in porous media and continuum thermodynamics. For porous media, it corresponds to the representative elementary volume [3] and it separates between coarse and smooth descriptions of the porous medium. For continuum thermodynamics, it corresponds to the elemental volume on

which the local equilibrium is valid [15, 28] and it separates between uniform and non-uniform description of the continuum. These two volumes both have their own length scale that depends on the structure of porous medium or the processes occurring inside. The hierarchy between the two length scales is not known *a priori*, they can be the same or one can be larger than the other. Nevertheless applying thermodynamic principles to porous media involves both length scales and the way they compare has a direct impact on the final macroscopic description.

One goal of modelling flows in porous media is the ability to perform numerical simulations, whose importance is constantly increasing in earth sciences and engineering. The expected advances concern the speed and accuracy of the simulations [8] but also their complexity by coupling multiple phenomena [27]. While improving the numerical methods is an active topic, the models used for simulating flows in porous media are generally not based on thermodynamics: Darcy's law is initially an empirical law and its extensions are mainly based on hydrodynamic arguments; the relative permeability that adapts Darcy's law for multiphase flow lacks theoretical foundations and satisfactory agreement with experiment; heat transfer, diffusion or chemical reactions are generally superimposed to the flow, using equations obtained by analogy with those governing the same phenomena in a continuous medium. Thus these models are exposed to some thermodynamic inconsistencies that can be the root of inherent biases and numerical difficulties. Concerning the coupling with other phenomena, the thermodynamic modelling has proven its relevance for the interactions between poro-mechanics and flows [12]. Reactive transport is an other active topic that could exploit a proper modelling of compositional flows [41]. Finally, numerous formulations [1, 5, 6, 10, 11, 22, 25, 37] have been developed to address the particularities of multiphase flow, like appearance and disappearance of fluid phases or switching between parabolic, elliptic and hyperbolic behaviors. They collectively show how to deal with multiphase flows but they are *ad hoc* constructions, difficult to generalize. A mathematical formulation of flows in porous media derived from thermodynamic principles would be more generic, ensure consistency, hopefully also when properly coupled with other phenomena, and could moreover benefit from the mathematical tools developed over times for thermodynamic systems.

This work proposes a derivation of macroscopic equations for multiphase flow in porous media. A strong assumption is that local equilibrium applies at the representative elementary volume. This means there is a length scale at which the thermodynamic quantities are uniform and the porous medium is seen as a smooth continuum. Although it is mostly suited to slow flows that are close to equilibrium, this assumption proves to be sufficient to recover most of the classical models. At first, the porous system is divided into distinct parts and the classical relations of equilibrium thermodynamics are reminded for each one. Next, the balance equation for entropy is derived from the matter and energy conservation principles and the local equilibrium of each part of the porous system. The entropy production is then analyzed to identify the different processes and, with additional assumptions, phenomenological laws are formulated for each processes. The resulting model describes an arbitrary number of phases, made of an arbitrary number of components, flowing through the porous media, subject to dissolution and to changes of phase, and constrained by capillarity. The analysis of the entropy production additionally provides new definitions for the equilibrium of the

system of interfaces and for the pressure-saturation relation that hold for systems with two phase or more. These definitions avoid involving ambiguous quantities like average interface curvature or average contact angle and they introduce new constraints for the pressure-saturation relation. In order to demonstrate the practicality of the full model, a mathematical formulation of the model is developed. It takes the form of a system of elliptic-parabolic differential equations whose main properties are: a persistent set of primary variables, a symmetric positive structure and a trivially associated entropy equation.

2. Description of the porous medium system

This work adopts a description of the porous medium and its content as a continuum. At each point of this macroscale continuum, the different parts of the porous system are independently at local equilibrium and are governed by their own equations of state. This section details the assumptions and the notations of that description.

2.1. Partitioning the system

Any volume, \mathcal{V} , of the porous medium system is assumed to be divided between the volume of the rock matrix (the solid phase), \mathcal{V}_r , and the volume of each fluid phase $\alpha \in \mathcal{P}$, \mathcal{V}_α . Here, \mathcal{P} denotes the set of indices for all the possible fluid phases. The fluid phase $\alpha \in \mathcal{P}$ is said missing in the system volume \mathcal{V} when $\mathcal{V}_\alpha = \emptyset$. In the following, the fluids are assumed to always completely fill the pores: $\mathcal{V} = \bigcup_{k \in \mathcal{P} \cup \{r\}} \mathcal{V}_k$. The measure of these volumes are denoted by $V = |\mathcal{V}|$ and $V_k = |\mathcal{V}_k|$ for $k \in \mathcal{P} \cup \{r\}$. The interface area between two fluid or solid phases indexed by k and l is denoted by $A_{\{k,l\}} = |\partial\mathcal{V}_k \cap \partial\mathcal{V}_l|$. In the following, $\mathcal{I}(\mathcal{E}) = \{\{k, l\} \mid k \in \mathcal{E}, l \in \mathcal{E}, k \neq l\}$ will denote the set of all pairs of the given index set \mathcal{E} ; the index set of all interfaces is $\mathcal{I}(\mathcal{P} \cup \{r\})$. For a fixed system volume \mathcal{V} , the volume \mathcal{V}_α of the fluid $\alpha \in \mathcal{P}$ can change as the fluids flow through the porous medium. However, the solid phase will be assumed rigid in this work, meaning that \mathcal{V}_r can not change when \mathcal{V} is fixed. According to these definitions, the interfaces have no volume and

$$V = V_r + \sum_{\alpha \in \mathcal{P}} V_\alpha .$$

Each phase is made of one or more components and the same component can be found in different phases. \mathcal{C} denotes the set of indices for all the possible components and N^i denotes the total number of mole of the component $i \in \mathcal{C}$ in the system volume \mathcal{V} . In this work, all the components are assumed to be exclusively in the fluid phases. This means that components in the interfaces are neglected and that there is no exchange of matter with the rock matrix. By denoting N_α^i the number of mole of component $i \in \mathcal{C}$ in the volume \mathcal{V}_α of fluid phase $\alpha \in \mathcal{P}$, one get the relation

$$N^i = \sum_{\alpha \in \mathcal{P}} N_\alpha^i \quad \forall i \in \mathcal{C} .$$

Let U denote the internal energy contained in the system volume \mathcal{V} . The internal energy is defined as the total energy excluding the kinetic energy due to the motion of the whole

system and the potential energy due to external force fields [15]. As such, the internal energy of the system is the sum of the internal energy of its parts,

$$U = \sum_{k \in \mathcal{P} \cup \{r\}} U_k + \sum_{\{k,l\} \in \mathcal{I}(\mathcal{P} \cup \{r\})} U_{\{k,l\}},$$

where U_k denotes the internal energy in the volume \mathcal{V}_k of the phase $k \in \mathcal{P} \cup \{r\}$ and $U_{\{k,l\}}$ denotes the internal energy in the surface $\partial\mathcal{V}_k \cap \partial\mathcal{V}_l$ of the interface $\{k, l\} \in \mathcal{I}(\mathcal{P} \cup \{r\})$.

2.2. Equilibrium thermodynamics

For a given isolated thermodynamic system, the state of thermodynamic equilibrium is the time-invariant state in which we see no further physical or chemical change in the system [28]. Equilibrium thermodynamics describe the changes of state of the system between successive equilibria. In particular, the state of the system is specified in terms of state variables such as volume, mole numbers of components, internal energy or entropy. The first law of thermodynamics, that expresses the principle of energy conservation in term of total differential of functions of state, is the basis of the theory. This section presents the assumptions and the relations that describe the thermodynamic equilibrium of the different parts of the porous system.

2.2.1. Fluid phases

The first law of thermodynamics applied to a fluid phase gives

$$dU_\alpha = T_\alpha dS_\alpha - p_\alpha dV_\alpha + \sum_{i \in \mathcal{C}} \mu_\alpha^i dN_\alpha^i \quad \forall \alpha \in \mathcal{P}, \quad (1)$$

where S_α denotes the entropy of the fluid phase α in the volume \mathcal{V}_α . The relation (1) indicates that the internal energy of the fluid α is a function of the form $U_\alpha(S_\alpha, V_\alpha, (N_\alpha^i)_i)$. It also provides the physical meaning for the derivatives of this function: T_α is the temperature of the fluid α ; p_α is the pressure of the fluid α ; and μ_α^i is the chemical potential of the component i in the fluid α . Similarly to the volume V_α , the mole numbers N_α^i or the internal energy U_α , the entropy S_α is an extensive variable whereas the temperature T_α , the pressure p_α and the chemical potentials μ_α^i are intensive variables. Note that since the fluid in \mathcal{V}_α is at equilibrium, its intensive variables have uniform values across all the volume \mathcal{V}_α . By applying the Euler's homogeneous function theorem on relation (1) one get

$$U_\alpha = T_\alpha S_\alpha - p_\alpha V_\alpha + \sum_{i \in \mathcal{C}} \mu_\alpha^i N_\alpha^i \quad \forall \alpha \in \mathcal{P}. \quad (2)$$

By taking the differential of equation (2) and subtracting equation (1), one derives the Gibbs-Duhem relation

$$0 = S_\alpha dT_\alpha - V_\alpha dp_\alpha + \sum_{i \in \mathcal{C}} N_\alpha^i d\mu_\alpha^i \quad \forall \alpha \in \mathcal{P}. \quad (3)$$

Let Ω_α denotes the grand (canonical) potential of the fluid α in the volume \mathcal{V}_α defined by

$$\Omega_\alpha = U_\alpha - T_\alpha S_\alpha - \sum_{i \in \mathcal{C}} \mu_\alpha^i N_\alpha^i \quad \forall \alpha \in \mathcal{P}, \quad (4)$$

from equation (1), its differential is

$$d\Omega_\alpha = -S_\alpha dT_\alpha - p_\alpha dV_\alpha - \sum_{i \in C} N_\alpha^i d\mu_\alpha^i \quad \forall \alpha \in \mathcal{P}.$$

The extensive variables can be associated to volume quantities. Let c_α^i be the molar concentration of component $i \in C$ in the fluid phase $\alpha \in \mathcal{P}$, u_α the volume internal energy of the fluid phase $\alpha \in \mathcal{P}$, s_α the volume entropy of the fluid phase $\alpha \in \mathcal{P}$ and ω_α the volume grand potential of the fluid phase $\alpha \in \mathcal{P}$. These volume quantities are linked to their extensive counterparts by

$$N_\alpha^i = V_\alpha c_\alpha^i, \quad U_\alpha = V_\alpha u_\alpha, \quad S_\alpha = V_\alpha s_\alpha, \quad \Omega_\alpha = V_\alpha \omega_\alpha \quad \forall i \in C \quad \forall \alpha \in \mathcal{P}.$$

Using the volume quantities, the Gibbs-Duhem relation (3) can be written as

$$dp_\alpha = s_\alpha dT_\alpha + \sum_{i \in C} c_\alpha^i d\mu_\alpha^i \quad \forall \alpha \in \mathcal{P}. \quad (5)$$

The volume of fluid α can be scaled to the volume of the whole system to define the volume fraction ϕ_α by

$$\phi_\alpha = \frac{V_\alpha}{V} \quad \forall \alpha \in \mathcal{P}.$$

The amount of internal energy of the fluid α per unit of system volume is $U_\alpha/V = \phi_\alpha u_\alpha$. According to equation (2), we have

$$\phi_\alpha u_\alpha = \phi_\alpha T_\alpha s_\alpha - \phi_\alpha p_\alpha + \sum_{i \in C} \phi_\alpha \mu_\alpha^i c_\alpha^i \quad \forall \alpha \in \mathcal{P},$$

the differential of this relation gives

$$d(\phi_\alpha u_\alpha) = T_\alpha d(\phi_\alpha s_\alpha) - p_\alpha d\phi_\alpha + \sum_{i \in C} \mu_\alpha^i d(\phi_\alpha c_\alpha^i) + \phi_\alpha s_\alpha dT_\alpha - \phi_\alpha dp_\alpha + \sum_{i \in C} \phi_\alpha c_\alpha^i d\mu_\alpha^i,$$

which, using equation (5), reduces to

$$d(\phi_\alpha u_\alpha) = T_\alpha d(\phi_\alpha s_\alpha) - p_\alpha d\phi_\alpha + \sum_{i \in C} \mu_\alpha^i d(\phi_\alpha c_\alpha^i) \quad \forall \alpha \in \mathcal{P}. \quad (6)$$

Similarly, the amount of grand potential of the fluid α per unit of system volume is $\Omega_\alpha/V = \phi_\alpha \omega_\alpha$. According to equation (4), its differential satisfies

$$d(\phi_\alpha \omega_\alpha) = d(\phi_\alpha u_\alpha) - d(\phi_\alpha T_\alpha s_\alpha) - \sum_{i \in C} d(\phi_\alpha c_\alpha^i \mu_\alpha^i),$$

which, using equation (6), reduces to

$$d(\phi_\alpha \omega_\alpha) = -\phi_\alpha s_\alpha dT_\alpha - p_\alpha d\phi_\alpha - \sum_{i \in C} \phi_\alpha c_\alpha^i d\mu_\alpha^i \quad \forall \alpha \in \mathcal{P}. \quad (7)$$

2.2.2. Interfaces

The interfaces are assumed to only exchange heat and work but not matter. Moreover, considering one kind of interface $\{k, l\} \in \mathcal{P} \cup \{r\}$ in the system volume \mathcal{V} , we assume that the set of the interfaces between phases k and l is at equilibrium as a whole. Then, the first law of thermodynamics applied to the interface gives

$$dU_{\{k,l\}} = T_{\{k,l\}}dS_{\{k,l\}} + \gamma_{\{k,l\}}dA_{\{k,l\}} \quad \forall \{k, l\} \in \mathcal{I}(\mathcal{P} \cup \{r\}), \quad (8)$$

where $S_{\{k,l\}}$ denotes the entropy of the interface $\{k, l\}$ in the volume \mathcal{V} . The relation (8) indicates that the internal energy of the interface $\{k, l\}$ is a function of the form $U_{\{k,l\}}(S_{\{k,l\}}, A_{\{k,l\}})$ and that its derivatives are the temperature $T_{\{k,l\}}$ and the surface tension $\gamma_{\{k,l\}}$ of the interface $\{k, l\}$. According to the assumptions, all the interfaces between phases k and l in the system volume \mathcal{V} have the same temperature and the same surface tension. Applying the Euler's homogeneous function theorem gives

$$U_{\{k,l\}} = T_{\{k,l\}}S_{\{k,l\}} + \gamma_{\{k,l\}}A_{\{k,l\}} \quad \forall \{k, l\} \in \mathcal{I}(\mathcal{P} \cup \{r\}) \quad (9)$$

and the Gibbs-Duhem relation for the interfaces is obtained by subtracting the equation (8) to the differential of the equation (9)

$$0 = S_{\{k,l\}}dT_{\{k,l\}} + A_{\{k,l\}}d\gamma_{\{k,l\}} \quad \forall \{k, l\} \in \mathcal{I}(\mathcal{P} \cup \{r\}). \quad (10)$$

Let $\Omega_{\{k,l\}}$ denotes the grand potential of the interface $\{k, l\}$ in the system volume \mathcal{V} defined by

$$\Omega_{\{k,l\}} = U_{\{k,l\}} - T_{\{k,l\}}S_{\{k,l\}} \quad \forall \{k, l\} \in \mathcal{I}(\mathcal{P} \cup \{r\}), \quad (11)$$

from equation (8), its differential is

$$d\Omega_{\{k,l\}} = -S_{\{k,l\}}dT_{\{k,l\}} + \gamma_{\{k,l\}}dA_{\{k,l\}} \quad \forall \{k, l\} \in \mathcal{I}(\mathcal{P} \cup \{r\}).$$

Surface quantities are introduced by scaling the extensive variables to interface area. For each interface $\{k, l\} \in \mathcal{I}(\mathcal{P} \cup \{r\})$, let $u_{\{k,l\}}$ be the surface internal energy, $s_{\{k,l\}}$ the surface entropy and $\omega_{\{k,l\}}$ the the surface grand potential. The surface quantities satisfy

$$U_{\{k,l\}} = A_{\{k,l\}}u_{\{k,l\}}, \quad S_{\{k,l\}} = A_{\{k,l\}}s_{\{k,l\}}, \quad \Omega_{\{k,l\}} = A_{\{k,l\}}\omega_{\{k,l\}} \quad \forall \{k, l\} \in \mathcal{I}(\mathcal{P} \cup \{r\}).$$

Using the surface quantities, the Gibbs-Duhem relation (10) can be written as

$$d\gamma_{\{k,l\}} = -s_{\{k,l\}}dT_{\{k,l\}} \quad \forall \{k, l\} \in \mathcal{I}(\mathcal{P} \cup \{r\}). \quad (12)$$

The area of interface $\{k, l\}$ can be scaled by the volume of the whole system to define the density of interface area $a_{\{k,l\}}$ as

$$a_{\{k,l\}} = \frac{A_{\{k,l\}}}{V} \quad \forall \{k, l\} \in \mathcal{I}(\mathcal{P} \cup \{r\}).$$

The amount of internal energy of the interface $\{k, l\}$ per unit of system volume is $U_{\{k,l\}}/V = a_{\{k,l\}}u_{\{k,l\}}$. According to equation (9), we have

$$a_{\{k,l\}}u_{\{k,l\}} = a_{\{k,l\}}T_{\{k,l\}}s_{\{k,l\}} + a_{\{k,l\}}\gamma_{\{k,l\}} \quad \forall \{k, l\} \in \mathcal{I}(\mathcal{P} \cup \{r\}),$$

the differential of this relation gives

$$d(a_{\{k,l\}}u_{\{k,l\}}) = T_{\{k,l\}}d(a_{\{k,l\}}s_{\{k,l\}}) + \gamma_{\{k,l\}}da_{\{k,l\}} + a_{\{k,l\}}s_{\{k,l\}}dT_{\{k,l\}} + a_{\{k,l\}}d\gamma_{\{k,l\}},$$

which, using equation (12), reduces to

$$d(a_{\{k,l\}}u_{\{k,l\}}) = T_{\{k,l\}}d(a_{\{k,l\}}s_{\{k,l\}}) + \gamma_{\{k,l\}}da_{\{k,l\}} \quad \forall \{k, l\} \in \mathcal{I}(\mathcal{P} \cup \{r\}). \quad (13)$$

Similarly, the amount of grand potential of the interface $\{k, l\}$ per unit of system volume is $\Omega_{\{k,l\}}/V = a_{\{k,l\}}\omega_{\{k,l\}}$. According to equation (11), its differential satisfies

$$d(a_{\{k,l\}}\omega_{\{k,l\}}) = d(a_{\{k,l\}}u_{\{k,l\}}) - d(a_{\{k,l\}}T_{\{k,l\}}s_{\{k,l\}}),$$

which, using equation (13), reduces to

$$d(a_{\{k,l\}}\omega_{\{k,l\}}) = -a_{\{k,l\}}s_{\{k,l\}}dT_{\{k,l\}} + \gamma_{\{k,l\}}da_{\{k,l\}} \quad \forall \{k, l\} \in \mathcal{I}(\mathcal{P} \cup \{r\}). \quad (14)$$

2.2.3. Matrix

The rock matrix is assumed to be a non deformable phase, it only exchange heat but neither work nor matter. Under these assumptions, the first law of thermodynamics applied to the rock matrix gives

$$dU_r = T_r dS_r \quad (15)$$

where S_r denotes the entropy of the rock matrix in the system volume \mathcal{V} and T_r its temperature. A common way to describe a rigid solid is by using the concept of heat capacity. Let c_v be the volume heat capacity at constant volume of the rock matrix defined as

$$c_v(T_r) = \frac{1}{V} \left. \frac{\partial U_r}{\partial T_r} \right|_V. \quad (16)$$

The grand potential of the rock matrix is defined by

$$\Omega_r = U_r - T_r S_r$$

and, from equation (15), its differential is

$$d\Omega_r = -S_r dT_r. \quad (17)$$

Let u_r be the volume internal energy of the rock matrix and s_r the volume entropy that satisfy

$$U_r = V_r u_r, \quad S_r = V_r s_r.$$

Besides, let ϕ_r be the volume fraction of rock matrix such that

$$\phi_r = \frac{V_r}{V}.$$

Using ϕ_r , u_r and s_r , equations (15) and (16) give

$$\phi_r u_r = \int_0^{T_r} c_v(T) dT \quad \text{and} \quad \phi_r s_r = \int_0^{T_r} \frac{c_v(T)}{T} dT. \quad (18)$$

For a fixed system volume \mathcal{V} , one can derive from equations (15) and (17) that

$$d(\phi_r u_r) = T_r d(\phi_r s_r) \quad (19)$$

and

$$d(\phi_r \omega_r) = -\phi_r s_r dT_r . \quad (20)$$

2.3. Representative elementary volume and the continuum approach

Thermodynamics manages to describe systems with a large number of molecules by abandoning the molecular level description in favor of a larger scale description. As a consequence, there is a low limit on the size of a thermodynamic system. The same idea lies behind the concept of *representative elementary volume* (REV) for porous media [3]. At the pore scale, a porous medium exhibits a complex geometry and fluid volumes are difficult to track. A volume \mathcal{V} of the porous medium system could be considered a REV if it is smooth enough at the pore scale (*e.g.* a sphere) and if it is much larger than a single pore. For instance, regarding the porosity, \mathcal{V} must be large enough to minimize the fluctuations of the matrix volume fraction due to the random pore size distribution, however \mathcal{V} must also be small enough to lower the sensitivity of the volume fraction to large scale inhomogeneity. The same reasoning holds for other averaged quantities such as the content of mole of a component or the content of energy. This work assumes the existence a common concept of REV which remains relevant for all the considered averaged quantities. By introducing the concept of REV, the continuum approach replaces the actual medium and its pore scale heterogeneity by a fictitious continuum in which the averaged quantities have a value at any point of the domain.

2.4. Local equilibrium

As heat and fluids flow through the porous medium, the thermodynamic equilibrium can not be assumed for the porous medium system over the entire domain. Yet, thermodynamic quantities such as temperature or pressure remain relevant locally. The local equilibrium assumption states that equilibrium thermodynamic relations are valid for the thermodynamic variables assigned to an elemental volume [15, 28]. As a consequence, all intensive thermodynamic variables and volume quantities (densities) becomes functions of position and time. The local equilibrium is an efficient approximation for a wide range of hydrodynamic and chemical systems. The present work adopts this assumption in the context of porous media by using the concept of REV (section 2.3) as elemental volume.

In order to apply both the continuum approach and the local equilibrium to the equilibrium thermodynamics presented in section 2.2, we only retain the equations regarding intensive or averaged variables; namely equations (5), (6) and (7) for the fluids, equations (12), (13) and (14) for the interfaces, and equations (18), (19) and (20) for the matrix. According to the local equilibrium, all these equations are considered locally valid.

2.5. Equations of state of the parts of the system

An equation of state relates the state variables of a thermodynamic system such as its pressure, its temperature or its volume. Equations of state cannot be derived from the general relations of thermodynamics alone but require additional knowledge either from experimental measurements or theoretical considerations on the microscopic structure. An equation of state fully characterizes the thermodynamic behaviour of a substance however it can take various equivalent forms depending on the subset of state variables selected to express it.

Equation (18) is an equation of state for the rock matrix, provided that the function $c_v(T)$ is known. For each fluid phase α , the Gibbs-Duhem relation (5) suggests an equation of state of the form

$$p_\alpha(T_\alpha, (\mu_\alpha^i)_i).$$

Similarly, equation (12) suggests the form

$$\gamma_{\{k,l\}}(T_{\{k,l\}})$$

for the equation of state of the interface $\{k, l\}$. The proposed forms of equations of state rely on the assumptions made in this section on each part of the porous medium system, such as the matrix being non deformable or the interfaces not exchanging matter. It should be noted that knowing the equations of states for each part of the system is not sufficient to characterize the whole system. In particular, the volume fractions, ϕ_α , and the densities of interface area, $a_{\{k,l\}}$, remain uncontrolled.

3. Balance equations

The section 2 established a local description of the porous medium system. The space and time evolution of the system will be derived from conservation principles. Following the local description, the balance equations are expressed locally, in the form of partial derivative equations, for each part of the porous medium system.

3.1. Conservation of components

The general balance of component $i \in C$ in the the fluid phase $\alpha \in \mathcal{P}$ is

$$\frac{\partial \phi_\alpha c_\alpha^i}{\partial t} + \text{div } \varphi_\alpha^{n,i} = \Lambda_\alpha^{n,i}$$

where $\varphi_\alpha^{n,i}$ is the molar flux of component i in the fluid phase α and $\Lambda_\alpha^{n,i}$ is the molar production rate of component i in fluid phase α . The local production of component i in phase α can come from other species of the phase α or from other parts of the system (other fluids, matrix and interfaces). All these transformations can be described as chemical reactions [15, 28], the local component production being expressed in terms of reaction velocities v^j and stoichiometric coefficients $b_\alpha^{j,i}$:

$$\Lambda_\alpha^{n,i} = \sum_{j \in \text{reactions}} b_\alpha^{j,i} v^j.$$

In the current work, we are not taking in account the full range of possible chemical reactions but only component transfer from fluid phase to fluid phase. The local production terms then find a simpler expression,

$$\Lambda_\alpha^{n,i} = \sum_{\beta \in \mathcal{P}} \Lambda_{\alpha,\beta}^{n,i}$$

where $\Lambda_{\alpha,\beta}^{n,i}$ is the molar rate of component i received by fluid phase α from fluid phase β . By definition of the exchange term $\Lambda_{\alpha,\beta}^{n,i}$, one have

$$\Lambda_{\alpha,\beta}^{n,i} = -\Lambda_{\beta,\alpha}^{n,i} \quad \forall i \in \mathcal{C} \quad \forall \alpha \in \mathcal{P} \quad \forall \beta \in \mathcal{P}. \quad (21)$$

Furthermore, according to the assumptions of section 2, components are only present in the fluid phases, thus the conservation of components is fully described by the balances of component $i \in \mathcal{C}$ in fluid phase $\alpha \in \mathcal{P}$:

$$\frac{\partial \phi_\alpha c_\alpha^i}{\partial t} + \text{div} \varphi_\alpha^{n,i} = \sum_{\beta \in \mathcal{P}} \Lambda_{\alpha,\beta}^{n,i} \quad (22)$$

Let M^i denotes the molar mass of the component $i \in \mathcal{C}$, and ρ_α denotes the mass density of the phase $\alpha \in \mathcal{P}$, they satisfy

$$\rho_\alpha = \sum_{i \in \mathcal{P}} M^i c_\alpha^i. \quad (23)$$

We introduce the notion of mass average velocity [3, 4] of the phase α , \mathbf{q}_α , defined by

$$\rho_\alpha \mathbf{q}_\alpha = \sum_{i \in \mathcal{C}} M^i \varphi_\alpha^{n,i}, \quad (24)$$

where $\rho_\alpha \mathbf{q}_\alpha$ represents the momentum per unit volume of the phase α . The part of the molar flux not due to the phase velocity is defined by

$$\mathbf{J}_\alpha^{n,i} = \varphi_\alpha^{n,i} - c_\alpha^i \mathbf{q}_\alpha. \quad (25)$$

$\mathbf{J}_\alpha^{n,i}$ is called the molar diffusive flux (relative to mass average velocity) of the component $i \in \mathcal{C}$ in the fluid phase $\alpha \in \mathcal{P}$. From equations (23), (24) and (25), the diffusive fluxes in the fluid α satisfy

$$\sum_{i \in \mathcal{C}} M^i \mathbf{J}_\alpha^{n,i} = 0 \quad \forall \alpha \in \mathcal{P}.$$

The total balance equation for component $i \in \mathcal{C}$ is obtained by summing equation (22) over all the fluid phases. Using equations (21) and (25), we get

$$\frac{\partial n^i}{\partial t} + \text{div} \left(\sum_{\alpha \in \mathcal{P}} c_\alpha^i \mathbf{q}_\alpha + \mathbf{J}_\alpha^{n,i} \right) = 0 \quad \forall i \in \mathcal{C} \quad (26)$$

with

$$n^i = \sum_{\alpha \in \mathcal{P}} \phi_\alpha c_\alpha^i \quad \forall i \in \mathcal{C}. \quad (27)$$

The *continuity equation* is obtained by multiplying the equations (26) by the molar mass M^i then summing over the components:

$$\frac{\partial}{\partial t} \left(\sum_{\alpha \in \mathcal{P}} \phi_\alpha \rho_\alpha \right) + \operatorname{div} \left(\sum_{\alpha \in \mathcal{P}} \rho_\alpha \mathbf{q}_\alpha \right) = 0 .$$

3.2. Balance of internal energy

The principle of energy conservation does not apply to internal energy but to total energy (sum of internal energy, kinetic energy and potential energy). Nonetheless a balance equation for the internal energy can be obtained at the microscopic scale by subtracting the balance equation of mechanical energy to the total energy conservation [4, 15]. Averaging the internal energy balance over the REV is non trivial, especially because of the non linear contributions of the velocity, and several authors have proposed macroscopic balance equations for the internal energy [3, 9, 21, 29, 44]. Unfortunately, the various propositions are not equivalent, neither are they all compatible. Here, we use a simplified balance of internal energy where the only remaining velocity-related contributions are all linear. This is relevant for flow regimes where velocities at pore scale are small enough to neglect high order contributions.

Considering the creeping flow regime [4] at the REV scale, we can neglect inertia effects like kinetic energy and viscous dissipation against internal energy, compression effects, heat diffusion and gravity work. According to this assumption and those of section 2, the balance of internal energy for the fluid phase $\alpha \in \mathcal{P}$ takes the form:

$$\frac{\partial \phi_\alpha u_\alpha}{\partial t} + \operatorname{div}(h_\alpha \mathbf{q}_\alpha + \mathbf{J}_\alpha^u) = \sum_{p' \in \mathcal{P} \cup \{r\} \cup \mathcal{I}(\mathcal{P} \cup \{r\})} \Lambda_{\alpha, p'}^u + \rho_\alpha \mathbf{q}_\alpha \cdot \mathbf{g} . \quad (28)$$

Where h_α is the volume enthalpy of fluid phase α , \mathbf{J}_α^u is the heat flux through fluid phase α , $\Lambda_{\alpha, p'}^u$ is the volume rate of energy received by fluid phase α from the part p' of the porous system, and \mathbf{g} is the gravitational acceleration. The volume enthalpy of the fluid α is related to its internal energy and its pressure by

$$h_\alpha = u_\alpha + p_\alpha ,$$

meaning that the term $\operatorname{div}(h_\alpha \mathbf{q}_\alpha)$ of equation (28) gathers two contributions: the internal energy advection, $\operatorname{div}(u_\alpha \mathbf{q}_\alpha)$, and the reversible compression work, $\operatorname{div}(p_\alpha \mathbf{q}_\alpha)$. The last term of equation (28), $\rho_\alpha \mathbf{q}_\alpha \cdot \mathbf{g}$, is the reversible work of the force of gravity on the fluid α .

As the rock matrix is assumed to be no deformable and to only exchange heat but not work, its balance of internal energy is simpler to establish and take the form

$$\frac{\partial \phi_r u_r}{\partial t} + \operatorname{div}(\mathbf{J}_r^u) = \sum_{p' \in \mathcal{P} \cup \{r\} \cup \mathcal{I}(\mathcal{P} \cup \{r\})} \Lambda_{r, p'}^u . \quad (29)$$

Where \mathbf{J}_r^u is the heat flux through the solid phase, and $\Lambda_{r, p'}^u$ is the volume rate of energy received by the solid phase from the part p' of the porous system.

Since the transport by macroscopic displacement of the interfaces is not considered here, the balance of internal energy for the interface $\{k, l\} \in \mathcal{I}(\mathcal{P} \cup \{r\})$ take a similar form

$$\frac{\partial a_{\{k,l\}} u_{\{k,l\}}}{\partial t} + \text{div}(\mathbf{J}_{\{k,l\}}^u) = \sum_{p' \in \mathcal{P} \cup \{r\} \cup \mathcal{I}(\mathcal{P} \cup \{r\})} \Lambda_{\{k,l\}, p'}^u. \quad (30)$$

Where $\mathbf{J}_{\{k,l\}}^u$ is the heat flux through the interface $\{k, l\}$, and $\Lambda_{\{k,l\}, p'}^u$ is the volume rate of energy received by the interface $\{k, l\}$ from the part p' of the porous system.

In equations (28), (29) and (30), the terms $\Lambda_{p,p'}^u$ encompass all the energy exchanges that occur between the parts p and p' of the system $\mathcal{P} \cup \{r\} \cup \mathcal{I}(\mathcal{P} \cup \{r\})$. The origin of these exchanges can be heat, work, matter or a combination of these. By definition of the exchange terms, it holds that

$$\Lambda_{p,p'}^u = -\Lambda_{p',p}^u \quad \forall p \in \mathcal{P} \cup \{r\} \cup \mathcal{I}(\mathcal{P} \cup \{r\}) \quad \forall p' \in \mathcal{P} \cup \{r\} \cup \mathcal{I}(\mathcal{P} \cup \{r\}). \quad (31)$$

Thanks to (31), summing the equations (28), (29) and (30) gives the following balance of internal energy for the mixture

$$\frac{\partial u}{\partial t} + \text{div} \left(\sum_{\alpha \in \mathcal{P}} h_\alpha \mathbf{q}_\alpha + \sum_{p \in \mathcal{P} \cup \{r\} \cup \mathcal{I}(\mathcal{P} \cup \{r\})} \mathbf{J}_p^u \right) = \sum_{\alpha \in \mathcal{P}} \rho_\alpha \mathbf{q}_\alpha \cdot \mathbf{g} \quad (32)$$

with

$$u = \sum_{\alpha \in \mathcal{P}} \phi_\alpha u_\alpha + \sum_{\{k,l\} \in \mathcal{I}(\mathcal{P} \cup \{r\})} a_{\{k,l\}} u_{\{k,l\}} + \phi_r u_r. \quad (33)$$

3.3. Balance of entropy

When considering an arbitrary thermodynamic system with entropy S , the variation of entropy dS can be written as the sum of the entropy supplied to the system by its surrounding, $d_e S$, and the entropy produced inside the system, $d_i S$: $dS = d_e S + d_i S$. The second law of thermodynamics states that $d_i S \geq 0$ for any transformation, the case $d_i S = 0$ corresponding to a reversible transformation. Following the continuum approach, this can be expressed locally and the local entropy production by unit volume must also be positive [15, 28]. For the porous medium system, the local form of the second law of thermodynamics may be written as

$$\frac{\partial s}{\partial t} + \text{div} \boldsymbol{\varphi}^s = \Psi \geq 0 \quad (34)$$

where s is the total volume entropy of the system, $\boldsymbol{\varphi}^s$ is the total entropy flux, and Ψ is the rate of local entropy production. The total entropy production Ψ includes the dissipative processes occurring in each part of the system but also those resulting from the interactions between the parts of the system; its expression is derived below.

Entropy being an extensive quantity, the total volume entropy of the system is the sum over the parts of the system:

$$s = \phi_r s_r + \sum_{\alpha \in \mathcal{P}} \phi_\alpha s_\alpha + \sum_{\{k,l\} \in \mathcal{I}(\mathcal{P} \cup \{r\})} a_{\{k,l\}} s_{\{k,l\}}. \quad (35)$$

By taking the time derivative of the sum and using the relations (6), (13) and (19), we get

$$\begin{aligned} \frac{\partial s}{\partial t} &= \frac{1}{T_r} \frac{\partial \phi_r u_r}{\partial t} \\ &+ \sum_{\alpha \in \mathcal{P}} \left[\frac{1}{T_\alpha} \frac{\partial \phi_\alpha u_\alpha}{\partial t} + \frac{p_\alpha}{T_\alpha} \frac{\partial \phi_\alpha}{\partial t} - \sum_{i \in \mathcal{C}} \frac{\mu_\alpha^i}{T_\alpha} \frac{\partial \phi_\alpha c_\alpha^i}{\partial t} \right] \\ &+ \sum_{\{k,l\} \in \mathcal{I}(\mathcal{P} \cup \{r\})} \left[\frac{1}{T_{\{k,l\}}} \frac{\partial a_{\{k,l\}} u_{\{k,l\}}}{\partial t} - \frac{\gamma_{\{k,l\}}}{T_{\{k,l\}}} \frac{\partial a_{\{k,l\}}}{\partial t} \right]. \end{aligned}$$

By using the notations

$$\begin{cases} \tau_p \equiv -1/T_p & \forall p \in \mathcal{P} \cup \{r\} \cup \mathcal{I}(\mathcal{P} \cup \{r\}) \\ \nu_\alpha^i \equiv \mu_\alpha^i/T_\alpha & \forall \alpha \in \mathcal{P} \forall i \in \mathcal{C} \end{cases} \quad (36)$$

and substituting the energy and mole balance equations (28), (30), (29) and (22), it comes

$$\begin{aligned} \frac{\partial s}{\partial t} &= - \sum_{p,p' \in \mathcal{P} \cup \{r\} \cup \mathcal{I}(\mathcal{P} \cup \{r\})} \tau_p \Lambda_{p,p'}^u - \sum_{i \in \mathcal{C}} \sum_{\alpha, \beta \in \mathcal{P}} \nu_\alpha^i \Lambda_{\alpha, \beta}^{n,i} \\ &+ \sum_{p \in \mathcal{P} \cup \{r\} \cup \mathcal{I}(\mathcal{P} \cup \{r\})} \tau_p \operatorname{div} \mathbf{J}_p^u + \sum_{i \in \mathcal{C}} \sum_{\alpha \in \mathcal{P}} \nu_\alpha^i \operatorname{div} \mathbf{J}_\alpha^{n,i} \\ &\sum_{\alpha \in \mathcal{P}} \left[\tau_\alpha \operatorname{div}(h_\alpha \mathbf{q}_\alpha) + \sum_{i \in \mathcal{I}(\mathcal{P} \cup \{r\})} \nu_\alpha^i \operatorname{div}(c_\alpha^i \mathbf{q}_\alpha) - \tau_\alpha \rho_\alpha \mathbf{g} \cdot \mathbf{q}_\alpha \right] \\ &+ \sum_{\alpha \in \mathcal{P}} \frac{p_\alpha}{T_\alpha} \frac{\partial \phi_\alpha}{\partial t} - \sum_{\{k,l\} \in \mathcal{I}(\mathcal{P} \cup \{r\})} \frac{\gamma_{\{k,l\}}}{T_{\{k,l\}}} \frac{\partial a_{\{k,l\}}}{\partial t}. \end{aligned}$$

The equation can be simplified and written in the form (34) by using the divergence of the scalar-vector product, the anti-symmetry of the $\Lambda_{p,p'}$ exchange coefficients and the fact that the relation (5) is equivalent to

$$\frac{1}{T_\alpha} dp_\alpha = h_\alpha d\tau_\alpha + \sum_{i \in \mathcal{C}} c_\alpha^i d\nu_\alpha^i.$$

Finally, the entropy flux is given by

$$\boldsymbol{\varphi}^s = - \sum_{p \in \mathcal{P} \cup \{r\} \cup \mathcal{I}(\mathcal{P} \cup \{r\})} \tau_p \boldsymbol{\varphi}_p^u - \sum_{\alpha \in \mathcal{P}} \sum_{i \in \mathcal{C}} \nu_\alpha^i \boldsymbol{\varphi}_\alpha^{n,i} \quad (37)$$

where

$$\begin{aligned} \boldsymbol{\varphi}_\alpha^u &= h_\alpha \mathbf{q}_\alpha + \mathbf{J}_\alpha^u \\ \boldsymbol{\varphi}_{\{k,l\}}^u &= \mathbf{J}_{\{k,l\}}^u \\ \boldsymbol{\varphi}_r^u &= \mathbf{J}_r^u, \end{aligned}$$

and the entropy production is given by

$$\begin{aligned}
\Psi = & -\frac{1}{2} \sum_{p,p' \in \mathcal{P} \cup \{r\} \cup \mathcal{I}(\mathcal{P} \cup \{r\})} \Lambda_{p,p'}^u (\tau_p - \tau_{p'}) - \frac{1}{2} \sum_{i \in \mathcal{C}} \sum_{\alpha, \beta \in \mathcal{P}} \Lambda_{\alpha, \beta}^{n,i} (v_\alpha^i - v_\beta^i) \\
& - \sum_{p \in \mathcal{P} \cup \{r\} \cup \mathcal{I}(\mathcal{P} \cup \{r\})} \mathbf{J}_p^u \cdot \nabla \tau_p - \sum_{\alpha \in \mathcal{P}} \sum_{i \in \mathcal{C}} \mathbf{J}_\alpha^{n,i} \cdot \nabla v_\alpha^i \\
& - \sum_{\alpha \in \mathcal{P}} \frac{1}{T_\alpha} \mathbf{q}_\alpha \cdot (\nabla p_\alpha - \rho_\alpha \mathbf{g}) \\
& + \sum_{\alpha \in \mathcal{P}} \frac{p_\alpha}{T_\alpha} \frac{\partial \phi_\alpha}{\partial t} - \sum_{\{k,l\} \in \mathcal{I}(\mathcal{P} \cup \{r\})} \frac{\gamma_{\{k,l\}}}{T_{\{k,l\}}} \frac{\partial a_{\{k,l\}}}{\partial t}.
\end{aligned} \tag{38}$$

The expression (37) of φ^s is similar to the usual form found in general literature [15, 28] while the equation (38) for the entropy production Ψ is very specific to flows in porous media. The next section is devoted to the analysis of the different terms of Ψ .

4. Entropy production: equilibria and linear regime

An expression (38) of the entropy production, $\Psi \geq 0$, has been derived in the previous section for a wide range of flows in porous media. The positivity of Ψ constrains the set of acceptable phenomenological laws that can be chosen to model flows. With additional assumptions, analysing the entropy production provides more precise constraints. This section studies the consequences of two simple modelling ideas: (i) the flow is slow enough to assume the different parts of the system are locally at equilibrium; (ii) the flow is slow enough to assume the system is spatially close to equilibrium and follows the linear regime.

4.1. The symmetry principle

The symmetry principle [15, 28] is helpful to split the entropy production in independent terms. It is based on the idea that the causes cannot have more symmetries than their effects. Applied to the entropy production, it suggests to group the terms of the sum according to their symmetries and to impose the positivity for each group. For equation (38), three kinds of term are involved, each with a different kind and amount of symmetries: the terms with a scalar difference, the terms with a gradient and the terms with a time derivative. Rewriting the entropy production with these three groups gives

the following decomposition:

$$\begin{aligned}
\Psi &= \Psi_{\text{difference}} + \Psi_{\text{gradient}} + \Psi_{\text{time derivative}} \\
\Psi_{\text{difference}} &= -\frac{1}{2} \sum_{p,p' \in \mathcal{P} \cup \{r\} \cup \mathcal{I}(\mathcal{P} \cup \{r\})} \Lambda_{p,p'}^u (\tau_p - \tau_{p'}) - \frac{1}{2} \sum_{i \in \mathcal{C}} \sum_{\alpha, \beta \in \mathcal{P}} \Lambda_{\alpha, \beta}^{n,i} (v_\alpha^i - v_\beta^i) \geq 0 \\
\Psi_{\text{gradient}} &= - \sum_{p \in \mathcal{P} \cup \{r\} \cup \mathcal{I}(\mathcal{P} \cup \{r\})} \mathbf{J}_p^u \cdot \nabla \tau_p - \sum_{\alpha \in \mathcal{P}} \sum_{i \in \mathcal{C}} \mathbf{J}_\alpha^{n,i} \cdot \nabla v_\alpha^i \\
&\quad - \sum_{\alpha \in \mathcal{P}} \frac{1}{T_\alpha} \mathbf{q}_\alpha \cdot (\nabla p_\alpha - \rho_\alpha \mathbf{g}) \geq 0 \\
\Psi_{\text{time derivative}} &= \sum_{\alpha \in \mathcal{P}} \frac{p_\alpha}{T_\alpha} \frac{\partial \phi_\alpha}{\partial t} - \sum_{\{k,l\} \in \mathcal{I}(\mathcal{P} \cup \{r\})} \frac{\gamma_{\{k,l\}}}{T_{\{k,l\}}} \frac{\partial a_{\{k,l\}}}{\partial t} \geq 0.
\end{aligned} \tag{39}$$

4.2. The linear regime

The entropy production terms $\Psi_{\text{difference}}$ and Ψ_{gradient} of equation (39) have the general form

$$\Psi^x = \sum_y J_y^x F_y^x \geq 0$$

where J_y^x and F_{yz}^x are respectively called *flows* and *forces* in a general thermodynamics sense. At equilibrium, all the forces and the corresponding flows vanish. For a system close to equilibrium, the flows can be expected to be linear functions of the forces [15, 28]. Accordingly, the following relation between the flows and the forces is assumed:

$$J_y^x = \sum_z L_{yz}^x F_z^x.$$

Here the coefficients L_{yz}^x are called *phenomenological coefficients* and the matrix they form, $(L_{yz}^x)_{yz}$, is expected to be symmetric and positive definite [38]. The extra-diagonal coefficients describe how pairs of processes interact, they vanish when the two corresponding processes are assumed to be independent.

4.3. Phenomenological laws of transport processes

While the symmetry principle is a deep and general argument to motivate the uncoupling of some processes, we can use more ad-hoc assumptions to simplify the entropy production, especially the term Ψ_{gradient} from equation (39) that gathers all the transport processes. Here we will assume that there is no interaction between two transport processes occurring through different parts of the system. In addition, considering a moving fluid $\alpha \in \mathcal{P}$, we will assume that the flow process (\mathbf{q}_α) and the diffusive processes (\mathbf{J}_α^u and $(\mathbf{J}_\alpha^{n,i})_{i \in \mathcal{C}}$) are independent. These assumptions result in

splitting the term Ψ_{gradient} in several independently positive sub-terms:

$$\begin{aligned}
\Psi_{\text{gradient}} &= \Psi_r^J + \sum_{\{k,l\} \in \mathcal{I}(\mathcal{P} \cup \{r\})} \Psi_{\{k,l\}}^J + \sum_{\alpha \in \mathcal{P}} (\Psi_\alpha^J + \Psi_\alpha^q) \\
\Psi_r^J &= -\mathbf{J}_r^u \cdot \nabla \tau_r \geq 0 \\
\Psi_{\{k,l\}}^J &= -\mathbf{J}_{\{k,l\}}^u \cdot \nabla \tau_{\{k,l\}} \geq 0 \\
\Psi_\alpha^J &= -\mathbf{J}_\alpha^u \cdot \nabla \tau_\alpha - \sum_{i \in \mathcal{C}} \mathbf{J}_\alpha^{n,i} \cdot \nabla v_\alpha^i \geq 0 \\
\Psi_\alpha^q &= -\frac{1}{T_\alpha} \mathbf{q}_\alpha \cdot (\nabla p_\alpha - \rho_\alpha \mathbf{g}) \geq 0.
\end{aligned} \tag{40}$$

Under the assumptions of section 4.2, the following will establish and discuss the linear phenomenological laws modelling the fluxes involved in the mass and energy balance equations of section 3.

4.3.1. Fluid flow

According to the entropy production $\Psi_\alpha^q \geq 0$ of equation (40), the linear phenomenological law for the velocity of the fluid phase $\alpha \in \mathcal{P}$ is

$$\mathbf{q}_\alpha = -L_\alpha^q (\nabla p_\alpha - \rho_\alpha \mathbf{g}) \quad \text{with} \quad L_\alpha^q \geq 0. \tag{41}$$

This equation corresponds to the Darcy-Muskat law [30, 35, 36] with L_α^q as the mobility of the fluid α . The mobility is usually split between the absolute permeability of the matrix, \mathbb{K} , the relative permeability of the fluid in the matrix, k_α , and the dynamic viscosity of the fluid, μ_α :

$$L_\alpha^q = \frac{k_\alpha}{\mu_\alpha} \mathbb{K}.$$

This demonstrates that the Darcy-Muskat law is compatible with the principles of thermodynamics, as already shown by Marle in [31].

4.3.2. Heat conduction in matrix

According to the entropy production $\Psi_r^J \geq 0$ of equation (40), the linear phenomenological law for the heat conduction through the matrix is

$$\mathbf{J}_r^u = -L_r^u \nabla \tau_r \quad \text{with} \quad L_r^u \geq 0. \tag{42}$$

From the definition (36) of τ_r , this flux can be expressed with the gradient of temperature by

$$\mathbf{J}_r^u = -\frac{1}{T_r^2} L_r^u \nabla T_r$$

which corresponds to the well-known Fourier's law with $\frac{1}{T_r^2} L_r^u$ as effective conductivity for the matrix.

4.3.3. Heat conduction in interfaces

According to the entropy production $\Psi_{\{k,l\}}^J \geq 0$ of equation (40), the linear phenomenological law for the heat conduction through the interface $\{k, l\} \in I(\mathcal{P} \cup \{r\})$ is

$$\mathbf{J}_{\{k,l\}}^u = -L_{\{k,l\}}^u \nabla \tau_{\{k,l\}} \quad \text{with} \quad L_{\{k,l\}}^u \geq 0.$$

This contribution to the total heat flow appears in some references [23, 31] but is generally neglected. This approximation would correspond to $L_{\{k,l\}}^u = 0$.

4.3.4. Matter diffusion and heat conduction in fluids

According to the entropy production $\Psi_\alpha^J \geq 0$ of equation (40), the linear phenomenological law for the diffusion and conduction through the fluid $\alpha \in \mathcal{P}$ is

$$\begin{cases} \mathbf{J}_\alpha^u = -L_\alpha^{uu} \nabla \tau_\alpha - \sum_{j \in \mathcal{C}} L_\alpha^{un,j} \nabla v_\alpha^j \\ \mathbf{J}_\alpha^{n,i} = -L_\alpha^{nu,i} \nabla \tau_\alpha - \sum_{j \in \mathcal{C}} L_\alpha^{nn,ij} \nabla v_\alpha^j \quad \forall i \in \mathcal{C} \end{cases} \quad (43)$$

where the phenomenological coefficients form a symmetric positive definite matrix:

$$L_\alpha^J = \begin{pmatrix} L_\alpha^{uu} & \dots & L_\alpha^{un,j} & \dots \\ \vdots & \dots & \dots & \dots \\ L_\alpha^{nu,i} & \dots & L_\alpha^{nn,ij} & \dots \\ \vdots & \dots & \dots & \dots \end{pmatrix}.$$

Like for the rock matrix, the coefficient L_α^{uu} is related to the effective conductivity of the Fourier's law by $\frac{1}{T_\alpha^2} L_\alpha^{uu}$.

The diffusion of components in the fluid phase are not described by a classical Fick's law like $\mathbf{J}_\alpha^{n,i} = D_\alpha^i \nabla c_\alpha^i$. Instead, the equation (43) introduces the matrix L_α^{nn} that links all the diffusive fluxes, $(\mathbf{J}_\alpha^{n,i})_{i \in \mathcal{C}}$, to all the gradients of the chemical potentials, $(\nabla v_\alpha^i)_{i \in \mathcal{C}}$. While the Fick's law is a good approximation of some limiting cases, it does not satisfy equation (40) in general [28]. Other models, like the Maxwell-Stefan equation or some generalizations of the Fick's law [4, 43], are fully compatible with the thermodynamics of multi-component mixtures and can be described by the matrix L_α^{nn} .

Finally, the coefficients L_α^{nu} and L_α^{un} describe the cross-effects resulting from the interactions between heat and matter flows: the Soret effect, where heat flow drives a flow of matter; and the Dufour effect, where concentration gradients drive a heat flow.

Marle suggests in [31] that the flux $\mathbf{J}_\alpha^{n,i}$ is not simply the average over the REV of the molecular diffusion at pore scale but that it also includes dispersion effects due to the difference between convection at pore scale and its average over the REV. However the splitting assumed in equation (40) is not compatible with such cross-effect between \mathbf{q}_α and $\mathbf{J}_\alpha^{n,i}$. Besides, dispersion appears to be a non-linear effect that is negligible at small velocity, which makes the linear regime unable to correctly describe it. More suited assumptions are needed to properly take into account the dispersion effect.

4.4. Thermal and chemical local equilibria

According to the entropy production $\Psi_{\text{difference}}$ of equation (39), and neglecting all the cross-effects, the linear phenomenological laws for local exchanges are

$$\begin{aligned}\Lambda_{p,p'}^u &= -r_{p,p'}^u(\tau_p - \tau_{p'}), & r_{p,p'}^u &\geq 0 \quad \forall p, p' \in \mathcal{P} \cup \{r\} \cup \mathcal{I}(\mathcal{P} \cup \{r\}) \\ \Lambda_{\alpha,\beta}^{n,i} &= -r_{\alpha,\beta}^{n,i}(v_\alpha^i - v_\beta^i), & r_{\alpha,\beta}^{n,i} &\geq 0 \quad \forall i \in \mathcal{C} \quad \forall \alpha, \beta \in \mathcal{P}.\end{aligned}$$

Here, the phenomenological coefficients r are inversely proportional to the characteristic time of the corresponding exchange process.

When the flow through the porous media is slow enough, the exchange characteristic times are negligible ($r \rightarrow \infty$), then the different parts of the system can be assumed to be locally at equilibrium at any time. As the phenomenological coefficients r degenerate while the differences vanish, the above linear laws become unsuitable. Instead, under the assumption of thermal and chemical local equilibria, they are replaced by the identities:

$$\begin{aligned}\tau &= \tau_p \quad \forall p \in \mathcal{P} \cup \{r\} \cup \mathcal{I}(\mathcal{P} \cup \{r\}) \\ v^i &= v_\alpha^i \quad \forall \alpha \in \mathcal{P} \quad \forall i \in \mathcal{C}\end{aligned}\tag{44}$$

where τ and v^i denote the common values for the different parts of the system. By inverting the definitions (36), the equilibrium temperature and the equilibrium chemical potential of component i are defined by

$$T = \frac{1}{-\tau} \quad \text{and} \quad \mu^i = \frac{v^i}{-\tau} \quad \forall i \in \mathcal{C}.\tag{45}$$

Since the exchange terms can no longer be retrieved, the total balance equations (26) and (32) should be preferred over the partial balance equations (22), (28), (29) and (30).

4.5. Interface local equilibrium

When the thermal and chemical equilibria (44) is assumed, thanks to the equations (6), (13) and (19), and the definitions (27), (33), (35) and (45), the time variation of the total internal energy of the porous system takes the form

$$\frac{\partial u}{\partial t} = T \frac{\partial s}{\partial t} + \sum_{i \in \mathcal{C}} \mu^i \frac{\partial n^i}{\partial t} - \Delta W_I\tag{46}$$

with

$$\Delta W_I \equiv \sum_{\alpha \in \mathcal{P}} p_\alpha \frac{\partial \phi_\alpha}{\partial t} - \sum_{\{k,l\} \in \mathcal{I}(\mathcal{P} \cup \{r\})} \gamma_{\{k,l\}} \frac{\partial a_{\{k,l\}}}{\partial t}.\tag{47}$$

This form is similar to that of a simple homogeneous system but corrected by ΔW_I . Here, $p_\alpha \partial_t \phi_\alpha$ represents the rate of mechanical work given by the fluid $\alpha \in \mathcal{P}$ and $\gamma_{\{k,l\}} \partial_t a_{\{k,l\}}$ the rate of mechanical work received by the interface $\{k, l\} \in \mathcal{I}(\mathcal{P} \cup \{r\})$. Like so, ΔW_I summarizes the exchanges of mechanical work between fluids and interfaces. Thanks to equation (39), this term is also directly connected to the entropy production:

$$\Delta W_I = T \Psi_{\text{time derivative}} \geq 0.$$

Thus ΔW_I is a dissipation term, that counts for the mechanical deformations and displacements of the interfaces. It is specific to multiphase flows since ΔW_I vanishes when there is only one fluid phase ($\text{Card}(\mathcal{P}) = \text{Card}(\mathcal{I}(\mathcal{P} \cup \{r\})) = 1$) with a not deformable matrix. When $\Delta W_I = 0$, the interface transformations are reversible and the interfaces are at equilibrium throughout the entire process. When $\Delta W_I > 0$, the transformations are irreversible and the interfaces are out of equilibrium.

The assumption of local equilibrium for the interfaces means the system evolves under the constraint $\Delta W_I = 0$ at any time. Since all the transformations of the system satisfy this equality, the time derivatives of equation (47) can be converted into total derivatives to give the following constraint:

$$\sum_{\alpha \in \mathcal{P}} p_\alpha d\phi_\alpha = \sum_{\{k,l\} \in \mathcal{I}(\mathcal{P} \cup \{r\})} \gamma_{\{k,l\}} da_{\{k,l\}} . \quad (48)$$

Equation (48) is an alternative definition of the local equilibrium of the interfaces. The next section explores how it can help to understand capillary effects.

5. Capillarity

Capillary effects are complex, they arise from the surface interactions between, at least, three phases: the matrix and two fluids. Their thermodynamic bases have been explored in past decades [18, 24, 33]. These works rely on the Young-Laplace equation that relates the pressure difference from either side of an interface to its curvature or, for spherical meniscus, to the contact angle. The drawback of this mechanical approach is to require some upscaling procedure to fully establish a model. Indeed, the Young-Laplace equation is essentially a pore scale relationship and the interface curvature or the contact angle have no meaning at REV scale.

The analysis developed here do not rely on such pore scale closure equation. Instead, it studies the interface dissipation $\Delta W_I \geq 0$ defined at equation (47) to show that the capillary pressure curve (53) is a general consequence of the interface equilibrium as expressed in equation (48). This result holds for system with more than two fluids and gives constraints on what are compatible multiphase capillary curves. The case of the dissipative interface transformations is then discussed and connected to more complex behaviours like the dynamical capillary pressure or the drainage-imbibition hysteresis.

5.1. Grand potential of the fluid mixture

A useful quantity to carry out the analysis of ΔW_I is the total volume grand potential of the fluid mixture,

$$\omega_f = \sum_{\alpha \in \mathcal{P}} \phi_\alpha \omega_\alpha + \sum_{\{k,l\} \in \mathcal{P} \cup \{r\}} a_{\{k,l\}} \omega_{\{k,l\}} .$$

Here, the name *fluid mixture* designates the whole system minus the matrix part, or equivalently the subsystem composed by all the fluids and all the interfaces in the system volume. Using the equations (47), (12), (7) and (14), the time variation of ω_f follows

$$\partial_t \omega_f = -s_I \partial_t T - \sum_{\alpha \in \mathcal{P}} \phi_\alpha \partial_t p_\alpha - \Delta W_I , \quad (49)$$

where s_I is the total volume entropy of the interfaces

$$s_I = \sum_{\{k,l\} \in \mathcal{P} \cup \{r\}} a_{\{k,l\}} s_{\{k,l\}} .$$

Like for the total internal energy in equation (46), ΔW_I appears as a dissipative term that indicates the difference in the system evolution depending on whether the interfaces follow reversible or irreversible processes.

5.2. Interface equilibrium and capillary pressure curve

Under the assumption of local equilibrium of the interfaces, ΔW_I vanishes and, thanks to equation (48), the variations of ω_f follow an equation stricter than (49):

$$d\omega_f = -s_I dT - \sum_{\alpha \in \mathcal{P}} \phi_\alpha dp_\alpha . \quad (50)$$

This relation indicates that the grand potential of the fluid mixture is a function of the temperature and fluid pressures: $\omega_f(T, (p_\alpha)_\alpha)$. The interface entropy s_I and the fluid volume fractions $(\phi_\alpha)_\alpha$ also become functions of the same variables, fully determined by the derivatives of $\omega_f(T, (p_\alpha)_\alpha)$:

$$\begin{aligned} s_I(T, (p_\alpha)_\alpha) &= -\frac{\partial \omega_f}{\partial T}(T, (p_\alpha)_\alpha) , \\ \phi_\alpha(T, (p_\beta)_\beta) &= -\frac{\partial \omega_f}{\partial p_\alpha}(T, (p_\beta)_\beta) \quad \forall \alpha \in \mathcal{P} . \end{aligned} \quad (51)$$

In other words, under the interface equilibrium assumption, s_I and $(\phi_\alpha)_\alpha$ are state variables and $\omega_f(T, (p_\alpha)_\alpha)$ is an equation of state for the fluid mixture. This equation of state is subject to some constraints. The first constraint is concavity. It is a consequence of the equation (49) applied on small irreversible transformations between two equilibrium states y^1 and y^2 , which gives

$$\omega_f(y^2) - \omega_f(y^1) - \partial_y \omega_f(y^1) \cdot (y^2 - y^1) \approx - \int_1^2 \Delta W_I \leq 0 .$$

For instance, the concavity implies that $\frac{\partial \phi_\alpha}{\partial p_\alpha} \geq 0$: increasing the pressure of one fluid against the others tends to increase its volume fraction. The equation of state ω_f is also subject to the constraint

$$\sum_{\beta \in \mathcal{P}} \frac{\partial \omega_f}{\partial p_\beta}(T, (p_\alpha)_\alpha) = -\phi$$

where $\phi = \sum_\alpha \phi_\alpha$ is the porosity, which is constant since the matrix is non deformable. This constraint also reads as the directional derivative

$$f'_{T, (p_\alpha)_\alpha} = -\phi \quad \text{with} \quad f_{T, (p_\alpha)_\alpha} : x \rightarrow \omega_f(T, (p_\alpha + x)_\alpha) .$$

Which gives by integration, for any pressure value p^0 ,

$$\omega_f(T, (p_\alpha + p^0)_\alpha) = \omega_f(T, (p_\alpha)_\alpha) - \phi p^0 . \quad (52)$$

Using this relation with a fixed p^0 in equation (51) shows that

$$\forall \beta \quad \phi_\beta(T, (p_\alpha + p^0)_\alpha) = \phi_\beta(T, (p_\alpha)_\alpha)$$

which means that the volume fractions do not depend on the absolute value of the pressures but only on their relative differences.

In the two phase case, with $\mathcal{P} = \{w, n\}$, the constraint (52) finds a simpler expression by introducing the function $F : x \rightarrow -\omega_f(T, 0, x)/\phi$. Equations (51) and (52) give the relation $\phi F'(p_n - p_w) = \phi_n(T, p_w, p_n)$ which takes a more usual form as

$$p_n - p_w = p_c(S_n) \quad \text{with} \quad S_n = \frac{\phi_n}{\phi} \quad \text{and} \quad p_c = (F')^{-1}. \quad (53)$$

This is the well known equation of the capillary pressure curve [7, 30]. The functions ω_f and p_c appears to be equivalent in the two phase case. This provides a thermodynamic interpretation to the capillary pressure curve based on the interface equilibrium and the non deformable matrix. Moreover, the thermodynamic approach naturally extends to any number of fluids and establishes that only one function, $\omega_f(T, (p_\alpha)_\alpha)$, is needed to capture the capillary behaviour of the multiphase system.

5.3. On dissipation in capillary processes

When the interface transformations are irreversible, the interfaces can no longer be considered at equilibrium during the system evolution. Interface equilibrium could still be reached as steady state, entropy being dissipated during the process. Or interfaces could be forced to jump between equilibrium states through irreversible transitions. In the followings, two kind of processes are considered. First, the relaxation towards equilibrium, where the system is out of, but still close to, equilibrium. In this case, the linear regime can be applied and gives a behavior of dynamic capillary pressure. Second, metastability at pore scale is discussed and linked to hysteresis behavior. In both cases, the dissipation in capillary processes invalidates the traditional capillary pressure curve (53) established under interface equilibrium and requires more elaborated relationship.

5.3.1. Relaxation towards equilibrium

Let ω_f^* , s_I^* and $(\phi_\alpha^*)_\alpha$ denote the value of ω_f , s_I and $(\phi_\alpha)_\alpha$ at steady state. If these values appear to be functions of the state $(T, (p_\alpha)_\alpha)$, then the steady state is considered to be an equilibrium state and ω_f^* , s_I^* and $(\phi_\alpha^*)_\alpha$ are state functions that follow the relation (50). In particular, the following equation holds

$$\frac{\partial \omega_f^*(T, (p_\alpha)_\alpha)}{\partial t} = -s_I^*(T, (p_\alpha)_\alpha) \frac{\partial T}{\partial t} - \sum_{\alpha \in \mathcal{P}} \phi_\alpha^*(T, (p_\alpha)_\alpha) \frac{\partial p_\alpha}{\partial t},$$

while the quantities ω_f , s_I and $(\phi_\alpha)_\alpha$ satisfy equation (49). Rearranging and subtracting the two gives a new expression for the entropy production due to dissipation at interface:

$$-\partial_t(\omega_f - \omega_f^*) - (s_I - s_I^*)\partial_t T - \sum_{\alpha \in \mathcal{P}} (\phi_\alpha - \phi_\alpha^*)\partial_t p_\alpha = \Delta W_I = T\Psi_{\text{time derivative}} \geq 0.$$

The dissipation find here a form more compatible with the *flow-force* products discussed in section 4.2. For a two-phase flow, $\mathcal{P} = \{n, w\}$, it becomes

$$-\partial_t(\omega_f - \omega_f^*) - (s_l - s_l^*)\partial_t T - (\phi_n - \phi_n^*)\partial_t(p_n - p_w) \geq 0 .$$

Assuming the system to be close to equilibrium and neglecting cross-effects, it suggests the following phenomenological law

$$\phi_n = \phi_n^* - A\partial_t(p_n - p_w), \quad A \geq 0 .$$

This corresponds to an alternative form of the dynamic capillary pressure described in [24, 26].

5.3.2. *Metastability and hysteresis*

When a system is driven by a cyclic variation of one external variable, the path it follows in the thermodynamic state space depends on the processes involved. If the transformations are reversible, the system state goes back and forth along a line of equilibrium states that connects the two extremal positions. If irreversible transformations occur, the path connecting the two extremal positions changes depending on its direction, such that, on a full cycle, the two paths form a loop. The presence of such loops is often referred as hysteresis but some distinctions are required. For instance, relaxation processes, like for the dynamic capillary pressure, cause a loop that is time-dependent: the slower is the transformation, the less it dissipates and the smaller is the amplitude of the loop. At extremely slow changes, the back and forth paths become indistinguishable: the loop disappears and the transformation can be approximated as reversible. However, there are systems that exhibit time-independent loop, like the drainage-imbibition cycle [34]. In this case, the paths are irreversible but also stable and reproducible. The irreversibility is highlighted by the existence of the scanning curves: at any point, reversing the changes on the system will not cause the system to take its previous path backward but a new path instead. All states on the paths are stable since the loop is time-independent. In particular, when stopping the external change, the system stays indefinitely in the same state.

The *domain theory* [16, 17, 19, 20] proposes a general thermodynamics understanding of the latter type of hysteresis, associated with time-independent loops. Two recent overview articles [2, 40], dedicated on modelling capillary hysteresis in porous media, develop its historical context and its extensions. The theory is general in the sense that it is not restricted to porous media: the hysteresis phenomenon is explained as the result of a large assembly of small metastable switches. Here, a system is said to be metastable for some given control variables when it possesses two, or more, stable equilibrium states at the same values of control variables. This is only possible if the system have internal, uncontrolled, variables. When the control variables change, the equilibrium states change too, each following its own branch. The metastable system can evolve reversibly on an equilibrium branch as long as the equilibrium is stable. If the equilibrium of a branch become unstable, the branch stops. A switch is a metastable system whose at least one equilibrium branch stops. When the switch state reaches a branch stop, it rapidly jumps to the remaining stable equilibrium state through an

irreversible and dissipative process. The domain theory shows that a system made of a large assembly of metastable switches, each slightly different from the others, presents the properties of hysteresis, like time-independent loops and scanning curves. The metastable switches contain elementary hysteresis, with discontinuous jumps, but the averaging over their large assembly generates the smooth, stable and reproducible loops.

For the hysteresis of the drainage-imbibition cycle, several mechanisms at pore scale have been considered as the main sources of hysteresis. The most regarded are the “ink bottle” effect, the “rain-drop” effect and the “snap-off” effect. (i) In the “ink bottle” effect [32], the only stable states for the pores are when they are filled with a unique fluid. The fluid-fluid interfaces are blocked at the bottle-necks and when the pressure difference around an interface reaches a threshold, the pore fills up rapidly with new fluid. The pores act as metastable switches where the interfaces jump between bottle-necks. (ii) The “rain drop” effect [14] designates the contact angle hysteresis that appears at the solid-fluid-fluid triple line. It is named after the shape taken by a drop flowing on a plate: the contact angles are different at the front and at the rear. Here, the smooth and stable hysteresis loop is already present at pore scale, thus it is expected to be also observed at large scale. The sources of the contact angle hysteresis are found in metastability in the triple line, caused for instance by surface roughness or adsorption. (iii) The “snap-off” effect [39, 42, 45] refers to the trapping of disconnected fluid. The effect is difficult to describe and model. For instance, the fact that fluid phases become disconnected weaken the assumption of one macroscopic pressure by phase. The metastability comes from the additional states the trapped fluid can reach.

6. A formulation for multiphase compositional flows

This section draws an explicit model for multiphase compositional flows in porous media from the developments above. First the existence of equations of state for the all porous system is discussed along with its consequences. Then the formulation is written as a system of partial differential equations.

The main assumptions of the model are: the matrix is inert and non deformable; no chemical reaction occurs, only change of phase of the components (vaporisation and dissolution); the porous system is always at local equilibrium; the molar and energy balance equations are given by the equations (26) and (32); the fluxes are given by the equations (41), (42) and (43). Here, the local equilibrium of the porous system means: local equilibrium for each part of the system taken separately (see section 2.4); thermal local equilibrium (see equation (44)); chemical local equilibrium (see equation (44)); interface local equilibrium (see equation (48)).

6.1. Equations of state of the porous system

Considering the equations of state $\omega_r(T)$, $\omega_f(T, (p_\alpha)_\alpha)$ and $(p_\alpha(T, (\mu^i)_i))_\alpha$ to be known, the grand potential of the porous system is the state function given by

$$\omega(T, (\mu^i)_i) = \phi_r \omega_r(T) + \omega_f(T, (p_\alpha(T, (\mu^i)_i))_\alpha) .$$

According to equations (5), (20) and (50), its differential satisfies

$$d\omega = -sdT - \sum_{i \in C} n^i d\mu^i .$$

Therefore, the total entropy of the porous is a function of the temperature and the chemical potentials: $s(T, (\mu_i)_i)$. Such an expression of the entropy is a first equation of state for the porous system, derived from the equations of state of the different parts of the system.

Some other equations of state are better related to the balance equations, thanks to the change of variables (45):

$$\tau = \frac{-1}{T} \quad \text{and} \quad v^i = \frac{\mu^i}{T} \quad \forall i \in C .$$

Indeed, with $(\tau, (v^i)_i)$ the Gibbs-Duhem relation (5) becomes

$$dp_\alpha = Th_\alpha d\tau + T \sum_{i \in C} c_\alpha^i dv^i \quad \forall \alpha \in \mathcal{P}$$

and $(\tau\omega)$ satisfies

$$d(\tau\omega) = u d\tau + \sum_{i \in C} n^i dv^i .$$

Hence the transported quantities, $(h_\alpha)_\alpha$ and $(c_\alpha^i)_{\alpha,i}$, and the conserved quantities, u and $(n^i)_i$, of the balance equations (26) and (32) become conjugate with the intensive variables $(\tau, (v^i)_i)$. More particularly, $(\tau\omega)$ as a function of $(\tau, (v^i)_i)$ appears to be the Legendre transform of the total entropy of the system:

$$\tau\omega - \tau u - \sum_{i \in C} v_i n_i = \frac{1}{T} \left(-\omega + u + \sum_{i \in C} \mu_i n_i \right) = s$$

with

$$ds = -\tau du - \sum_{i \in C} v^i dn^i .$$

This provides a new equation of state for the system, $s(u, (n^i)_i)$, expressed in term of total averaged variables rather than intensive variables like with $s(T, (\mu^i)_i)$ or $(\tau\omega)(\tau, (v^i)_i)$. An other consequence is the existence of a bijection between the sets of variables $(\tau, (v^i)_i)$ and $(u, (n^i)_i)$ when the equations of state are smooth.

While the equations of state must be convex, they are not necessarily smooth. In particular, ω_f will have non differentiable points when the associated capillary pressure curve accepts a range of saturation values for the same capillary pressure. In this case, the total derivatives should be replaced by subdifferentials, and the bijection between $(\tau, (v^i)_i)$ and $(u, (n^i)_i)$ should be replaced by the fact that $(\tau, (v^i)_i, u, (n^i)_i)$ belong to a $(1 + \text{Card}(C))$ -dimensional manifold.

6.2. Elliptic-parabolic differential equations

Let $n = 1 + \text{Card}(C)$ denote the number of unknowns of the problem and $d = 1, 2$ or 3 the space dimension. Now let $v \in \mathbb{R}^n$ be the vector of primary variables defined by $v = (v_i)_{i \in \{0\} \cup C}$ with

$$v_i = \begin{cases} \tau & \text{if } i = 0 \\ v_i & \text{if } i \in C \end{cases} .$$

The balance equations for the internal energy of the system and the total number of moles of each component can be written as a system of n elliptic-parabolic partial differential equations:

$$\frac{\partial B_i(v)}{\partial t} - \operatorname{div} \left(\sum_{j \in \{0\} \cup C} A_{i,j}(v) \nabla v_j - C_i(v) \right) = F_i(v, \nabla v) \quad \forall i \in \{0\} \cup C. \quad (54)$$

Here $B(v) \in \mathbb{R}^n$ and $F(v, \nabla v) \in \mathbb{R}^n$ are vectors of scalars, $C(v) \in (\mathbb{R}^d)^n$ is a vector of vectors and $A(v) \in (\mathbb{R}^{d \times d})^{n \times n}$ is a matrix of tensor. These coefficients are defined in the following, where the dependency of the physical quantities to the primary variables, v , is omitted to lighten the reading.

$B(v)$ is given by the derivatives of the convex function $(\tau\omega)$ with respect to v :

$$B_i(v) = \frac{\partial(\tau\omega)}{\partial v_i} \quad \forall i \in \{0\} \cup C. \quad (55)$$

$F(v, \nabla v)$ is given by

$$F_i(v, \nabla v) = \begin{cases} -\mathbf{g} \cdot \sum_{\alpha \in \mathcal{P}} \rho_\alpha L_\alpha^q \left(\sum_{i \in \{0\} \cup C} \frac{\partial p_\alpha}{\partial v_i} \nabla v_i - \rho_\alpha \mathbf{g} \right) & \text{if } i = 0 \\ 0 & \text{if } i \in C \end{cases}. \quad (56)$$

$C(v)$ is given by

$$C_i(v) = \sum_{\alpha \in \mathcal{P}} \frac{1}{T} \frac{\partial p_\alpha}{\partial v_i} \rho_\alpha L_\alpha^q \quad \forall i \in \{0\} \cup C. \quad (57)$$

$A(v)$ is given by

$$A_{i,j}(v) = A_{i,j}^u(v) + \sum_{\alpha \in \mathcal{P}} \left(L_{\alpha,i,j}^J + \frac{1}{T} \frac{\partial p_\alpha}{\partial v_i} \frac{\partial p_\alpha}{\partial v_j} L_\alpha^q \right) \quad \forall i, j \in \{0\} \cup C \quad (58)$$

where the $A_{i,j}^u(v)$ are tensors given by

$$A_{i,j}^u(v) = \begin{cases} L_r^u & \text{if } i = j = 0 \\ 0 & \text{if } i \in C \text{ or } j \in C \end{cases}.$$

The formulation (54)-(55)-(56)-(57)-(58) is fully characterized by the following inputs: the equations of state of the matrix, $\omega_r(T)$, of the fluids, $p_\alpha(T, (\mu^i)_i)$ with $\alpha \in \mathcal{P}$, and of the fluid mixture, $\omega_f(T, (p_\alpha)_\alpha)$; and the phenomenological coefficients for the conduction in the matrix, $L_r^u(v)$, for the conduction-diffusion in the fluids, $L_\alpha^J(v)$, and for the fluid velocities, $L_\alpha^q(v)$. All other quantities involved in the formulation can be retrieved from these inputs and the values of the primary variables v .

The formulation uses a persistent set of primary variables that does not depend on which phases are locally present. This feature has already been obtained for two-phase flows [1, 5, 6, 25, 37], but here it holds for an arbitrary numbers of phases and components, and no preferential phase is assumed. Besides, the system of equations (54) is well structured since the accumulation term $B(v)$ derives from a convex potential,

$(\tau\omega)(v)$, and the elliptic operator $A(v)$ is symmetric and positive. Furthermore, the entropy equation (34) is directly retrieved by summing the products of the equations (54) with the $(v_i)_i$. Among the others formulations [1, 5, 6, 10, 11, 22, 25, 37] that describe a comparable range of physical behaviors, the majority lacks this level of generality and none of them gather such structuring properties.

7. Concluding remarks

This paper applies the principles of the thermodynamics of irreversible processes to the representative elementary volume of a porous medium filled with multiple compositional fluids in order to model heat and mass transfers. A special attention has been taken to treat the interfaces in a consistent way. The physical assumptions made are usual and the resulting model does not present new macroscopic behaviors. Nevertheless, the final formulation exhibits less common, but useful, properties such as a persistent set of primary variables, a symmetric structure and an associated entropy equation.

One benefit of the thermodynamic approach is to avoid assuming specific processes at the microscopic scale, only that the system is close to equilibrium. This general framework turns out to be sufficient to justify macroscopic behaviors like the Darcy-Muskat law and the capillary pressure curve. The proposed explanation of capillarity in particular contrasts with the existing works that all rely on the Young-Laplace equation at pore scale. Moreover, it provides new and strong constraints on capillary pressure curve for three or more phases.

The physical assumptions made in this paper should be relaxed to include additional processes. For instance, taking the reactive chemistry into account could be of peculiar interest because chemistry has already a strong thermodynamic basis and the present work gives a thermodynamic understanding of flows in porous media. Formulating reactive transport on this common ground could help in properly solving this kind of coupling.

References

- [1] Abadpour, A., Panfilov, M., 2009. Method of negative saturations for modeling two-phase compositional flow with oversaturated zones. *Transport in porous media* 79 (2), 197–214.
- [2] Albers, B., 2014. Modeling the hysteretic behavior of the capillary pressure in partially saturated porous media: a review. *Acta Mechanica* 225 (8), 2163–2189.
- [3] Bear, J., 2013. *Dynamics of fluids in porous media*. Courier Corporation.
- [4] Bird, R. B., Stewart, W. E., Lightfoot, E. N., Klingenberg, D. J., 2015. *Introductory transport phenomena*. Wiley Global Education.
- [5] Bourgeat, A., Jurak, M., Smaï, F., 2009. Two-phase, partially miscible flow and transport modeling in porous media; application to gas migration in a nuclear waste repository. *Computational Geosciences* 13 (1), 29.

- [6] Bourgeat, A., Jurak, M., Smaï, F., 2013. On persistent primary variables for numerical modeling of gas migration in a nuclear waste repository. *Computational geosciences* 17 (2), 287–305.
- [7] Brooks, R., Corey, T., 1964. Hydraulic properties of porous media. *Hydrology Papers, Colorado State University* 24, 37.
- [8] Chen, Z., Huan, G., Ma, Y., 2006. *Computational methods for multiphase flows in porous media*. SIAM.
- [9] Cheng, P., 1979. Heat transfer in geothermal systems. In: *Advances in heat transfer*. Vol. 14. Elsevier, pp. 1–105.
- [10] Class, H., Helmig, R., Bastian, P., 2002. Numerical simulation of non-isothermal multiphase multicomponent processes in porous media.: 1. an efficient solution technique. *Advances in Water Resources* 25 (5), 533–550.
- [11] Coats, K. H., 1980. An equation of state compositional model. *Society of Petroleum Engineers Journal* 20 (05), 363–376.
- [12] Coussy, O., 2011. *Mechanics and physics of porous solids*. John Wiley & Sons.
- [13] Darcy, H. P. G., 1856. *Les Fontaines publiques de la ville de Dijon*. V. Dalamont.
- [14] De Gennes, P.-G., 1985. Wetting: statics and dynamics. *Reviews of modern physics* 57 (3), 827.
- [15] De Groot, S. R., Mazur, P., 2013. *Non-equilibrium thermodynamics*. Courier Corporation.
- [16] Enderby, J., 1955. The domain model of hysteresis. part 1.—independent domains. *Transactions of the Faraday Society* 51, 835–848.
- [17] Enderby, J., 1956. The domain model of hysteresis. part 2.—interacting domains. *Transactions of the Faraday Society* 52, 106–120.
- [18] Everett, D. H., 1975. Thermodynamics of multiphase fluids in porous media. *Journal of Colloid and Interface Science* 52 (1), 189–198.
- [19] Everett, D. H., Smith, F., 1954. A general approach to hysteresis. part 2: Development of the domain theory. *Transactions of the Faraday Society* 50, 187–197.
- [20] Everett, D. H., Whitton, W. I., 1952. A general approach to hysteresis. *Transactions of the Faraday Society* 48, 749–757.
- [21] Forsyth, P., 1994. Three-dimensional modelling of steam flush for dnapl site remediation. *International journal for numerical methods in fluids* 19 (12), 1055–1081.
- [22] Forsyth, P. A., Simpson, R., 1991. A two-phase, two-component model for natural convection in a porous medium. *International journal for numerical methods in fluids* 12 (7), 655–682.

- [23] Hassanizadeh, S. M., Gray, W. G., 1990. Mechanics and thermodynamics of multiphase flow in porous media including interphase boundaries. *Adv. Water Resour* 13 (4), 169–186.
- [24] Hassanizadeh, S. M., Gray, W. G., 1993. Thermodynamic basis of capillary pressure in porous media. *Water resources research* 29 (10), 3389–3405.
- [25] Jaffré, J., Sboui, A., 2010. Henry's law and gas phase disappearance. *Transport in porous media* 82 (3), 521–526.
- [26] Kalaydjian, F. J.-M., 1992. Dynamic capillary pressure curve for water/oil displacement in porous media: Theory vs. experiment. In: *SPE Annual Technical Conference and Exhibition*. Society of Petroleum Engineers, p. 491.
- [27] Kolditz, O., Görke, U.-J., Shao, H., Wang, W., 2012. Thermo-hydro-mechanical-chemical processes in porous media. Vol. 86. Springer-Verlag Berlin Heidelberg.
- [28] Kondepudi, D., Prigogine, I., 2014. *Modern thermodynamics: from heat engines to dissipative structures*. John Wiley & Sons.
- [29] Lake, L. W., 1989. *Enhanced oil recovery*. Old Tappan, NJ; Prentice Hall Inc.
- [30] Leverett, M., 1941. Capillary behavior in porous solids. *Transactions of the AIME* 142 (01), 152–169.
- [31] Marle, C., 1982. On macroscopic equations governing multiphase flow with diffusion and chemical reactions in porous media. *International Journal of Engineering Science* 20 (5), 643–662.
- [32] Miller, E. E., Miller, R. D., 1956. Physical theory for capillary flow phenomena. *Journal of Applied Physics* 27 (4), 324–332.
- [33] Morrow, N. R., 1970. Physics and thermodynamics of capillary action in porous media. *Industrial & Engineering Chemistry* 62 (6), 32–56.
- [34] Morrow, N. R., Harris, C. C., 1965. Capillary equilibrium in porous materials. *Society of Petroleum Engineers Journal* 5 (01), 15–24.
- [35] Muskat, M., Meres, M. W., 1936. The flow of heterogeneous fluids through porous media. *Physics* 7 (9), 346–363.
- [36] Muskat, M., Wyckoff, R., Botset, H., Meres, M., 1937. Flow of gas-liquid mixtures through sands. *Transactions of the AIME* 123 (01), 69–96.
- [37] Neumann, R., Bastian, P., Ippisch, O., 2013. Modeling and simulation of two-phase two-component flow with disappearing nonwetting phase. *Computational geosciences* 17 (1), 139–149.
- [38] Onsager, L., 1931. Reciprocal relations in irreversible processes. i. *Physical review* 37 (4), 405.

- [39] Schlüter, S., Berg, S., Rücker, M., Armstrong, R., Vogel, H.-J., Hilfer, R., Wildenschild, D., 2016. Pore-scale displacement mechanisms as a source of hysteresis for two-phase flow in porous media. *Water Resources Research* 52 (3), 2194–2205.
- [40] Schweizer, B., 2017. Hysteresis in porous media: Modelling and analysis. *Interfaces and Free Boundaries* 19 (3), 417–447.
- [41] Sin, I., Corvisier, J., 2019. Multiphase multicomponent reactive transport and flow modeling. *Reviews in Mineralogy and Geochemistry* 85 (1), 143–195.
- [42] Singh, K., Menke, H., Andrew, M., Lin, Q., Rau, C., Blunt, M. J., Bijeljic, B., 2017. Dynamics of snap-off and pore-filling events during two-phase fluid flow in permeable media. *Scientific reports* 7 (1), 1–13.
- [43] Taylor, R., 1993. *Multicomponent mass transfer*. Vol. 2. John Wiley & Sons.
- [44] Vafai, K., 2015. *Handbook of porous media*. CRC Press.
- [45] Wardlaw, N. C., 1982. The effects of geometry, wettability, viscosity and interfacial tension on trapping in single pore-throat pairs. *Journal of Canadian Petroleum Technology* 21 (03).