

A Thermodynamically Consistent Model for Compositional Multiphase Flows

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May 2023

Outline

- ▶ Applying the principles of non-equilibrium thermodynamics to flows in porous media
 - ▶ Assuming the Representative Elementary Volume (REV) is an elementary volume for local thermodynamic equilibrium
- ▶ Modelling thermal, multi-phase, multi-component flow
 - ▶ Miscible compressible fluids
 - ▶ No chemical reactions, rigid matrix
- ▶ Computing the total entropy of the system
- ▶ Discussing capillary effects

The porous medium system

Introduction

(not a) definition from [Bear, 1972]

▶ Multiple phases:

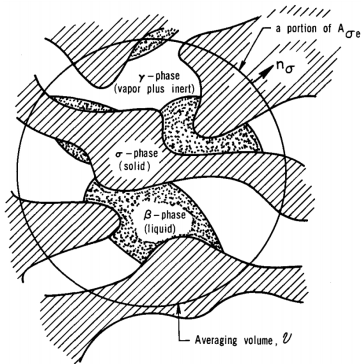
▶ Solid phase = Matrix

▶ One or more fluid phases fill the pore space

▶ Pore space is "relatively narrow" and matrix specific surface (S/V) is high

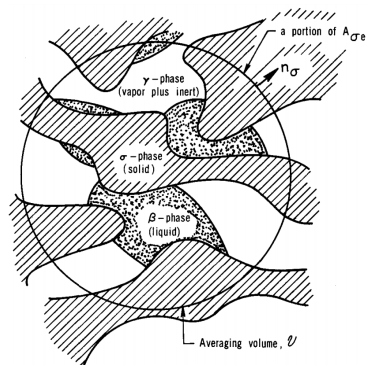
▶ a lot of interfaces

▶ Interconnected pore space: fluids flow within pores



The porous medium system

Description



- ▶ Components: $i \in \mathcal{C}$
- ▶ System parts:
 $k \in \mathcal{P} = \mathcal{P}^3 \cup \mathcal{P}^2 \cup \mathcal{P}^1$
 - \mathcal{P}^3 : matrix, fluids
 - \mathcal{P}^2 : interfaces
 - \mathcal{P}^1 : contact lines

▶ Extensive variables for each part

- ▶ Spatial extension X_k
 - volume $X_k = V_k, k \in \mathcal{P}^3$
 - interface area $X_k = A_k, k \in \mathcal{P}^2$
 - line length $X_k = L_k, k \in \mathcal{P}^1$
- ▶ Number of mole $N_k^i = X_k n_k^i$
- ▶ Internal energy $U_k = X_k u_k$
- ▶ Entropy $S_k = X_k s_k$

▶ Volume of porous system $V = \sum_{k \in \mathcal{P}^3} X_k$

- ▶ Averaged spatial extensions $x_k = \frac{X_k}{V}$
 - volume fraction $x_k = \phi_k, k \in \mathcal{P}^3$
 - area density $x_k = a_k, k \in \mathcal{P}^2$
 - length density $x_k = l_k, k \in \mathcal{P}^1$

The porous medium system

Equilibrium thermodynamics of homogeneous parts

- ▶ The equilibrium of each homogeneous part $k \in \mathcal{P}$ satisfies

$$S_k(U_k, (N_k^i)_i, X_k)$$

- ▶ The classical relations write as follows

$$d(x_k s_k) = -\tau_k d(x_k u_k) - \sum_i \nu_k^i d(x_k n_k^i) + \tau_k \omega_k dx_k \quad (\text{Gibbs/sys.})$$

$$ds_k = -\tau_k du_k - \sum_i \nu_k^i dn_k^i \quad (\text{Gibbs/part})$$

$$d(\tau_k \omega_k) = u_k d\tau_k + \sum_i n_k^i d\nu_k^i \quad (\text{Gibbs-Duhem})$$

- ▶ Intensive variables

- temperature
- chemical potential
- grand potential

$$T_k = -1/\tau_k$$

$$\mu_k^i = -\nu_k^i/\tau_k$$

$$\omega_k = \begin{cases} -p_k & \text{if } k \in \mathcal{P}^3 \text{ (pressure)} \\ \gamma_k & \text{if } k \in \mathcal{P}^2 \text{ (surface tension)} \end{cases}$$

Balance equations

Mole and energy

- ▶ Mole balance for $k \in \mathcal{P}$ and $i \in \mathcal{I}$

$$\frac{\partial x_k n_k^i}{\partial t} + \nabla \cdot \boldsymbol{\varphi}_k^{n,i} = \Lambda_k^{n,i}$$

- ▶ mass velocity: $\mathbf{q}_k = \rho_k^{-1} \sum_i M^i \boldsymbol{\varphi}_k^{n,i}$ with $\rho_k = \sum_i M^i n_k^i$
 - ▶ molar diffusion: $\mathbf{J}_k^{n,i} = \boldsymbol{\varphi}_k^{n,i} - n_k^i \mathbf{q}_k$
 - ▶ no reaction $\Rightarrow \sum_k \Lambda_k^{n,i} = 0$
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- ▶ Energy balance for $k \in \mathcal{P}$

$$\frac{\partial x_k u_k}{\partial t} + \nabla \cdot \boldsymbol{\varphi}_k^u = \Lambda_k^u + W_k^{\text{ext}}$$

- ▶ heat diffusion: $\mathbf{J}_k^u = \boldsymbol{\varphi}_k^u - h_k \mathbf{q}_k$ with $h_k = u_k - \omega_k$
- ▶ work of external forces: $W_k^{\text{ext}} = \mathbf{F}_k^{\text{ext}} \cdot \mathbf{q}_k$
- ▶ no reaction $\Rightarrow \sum_k \Lambda_k^u = 0$

Balance equations

Entropy

- ▶ The total entropy balance is computed as

$$\frac{\partial}{\partial t} \left(\sum_k x_k s_k \right) + \nabla \cdot \left(- \sum_k \tau_k \boldsymbol{\varphi}_k^u - \sum_{k,i} \nu_k^i \boldsymbol{\varphi}_k^{n,i} \right) = \Psi_{\text{scalar}} + \Psi_{\text{vector}} + \Psi_{\text{time}}$$

$$\Psi_{\text{scalar}} = - \sum_k \tau_k \Lambda_k^u - \sum_{k,i} \nu_k^i \Lambda_k^{n,i}$$

$$\begin{aligned} \Psi_{\text{vector}} = & - \sum_k \mathbf{J}_k^u \cdot \nabla \tau_k - \sum_{k,i} \mathbf{J}_k^{n,i} \cdot \nabla \nu_k^i \\ & - \sum_k \tau_k \mathbf{q}_k \cdot (\mathbf{F}_k^{\text{ext}} + \nabla \omega_k) \end{aligned}$$

$$\Psi_{\text{time}} = \sum_k \tau_k \omega_k \frac{\partial x_k}{\partial t}$$

- ▶ Second law: $\Psi_{\dots} \geq 0$ ($\Psi = 0 \rightarrow$ reversible process)
 - $\Psi_{\text{scalar}} = 0 \rightarrow$ local equilibrium: $\tau_k = \tau$, $\nu_k^i = \nu^i \quad \forall k \in \mathcal{P}$
 - $\Psi_{\text{vector}} \geq 0 \rightarrow$ dissipative transfert (Darcy, Fourier, ...)
 - $\Psi_{\text{time}} = 0 \rightarrow$ interface equilibrium: $\sum_k \omega_k dx_k = 0$

Equations of State for the porous system

- ▶ For each part k : $d(\omega_k) = \frac{h_k}{\tau} d\tau + \sum_i \frac{n_k^i}{\tau} d\nu^i$ (Gibbs-Duhem)
 - ▶ $\omega_k(\tau, (\nu^i)_i)$ is an equation of state for part k

- ▶ Using local and interface equilibrium, and introducing

$$s = \sum_k x_k s_k, \quad u = \sum_k x_k u_k, \quad n^i = \sum_k x_k n_k^i, \quad \omega = \sum_k x_k \omega_k$$

- ▶ $d\omega = \sum_k x_k d\omega_k$

- ▶ $ds = -\tau du - \sum_i \nu^i dn^i$ (like homogeneous system)

- ▶ $d(\tau\omega) = u d\tau + \sum_i n^i d\nu^i$ (conjugate of entropy)

- ▶ Assuming components are only in fluids

$$(k \in \mathcal{P}_{\text{fluid}} \Rightarrow x_k \omega_k = -\phi_k p_k)$$

$$d\omega = \frac{1}{\tau} h^{\text{non fluid}} d\tau - \sum_{k \in \mathcal{P}_{\text{fluid}}} \phi_k dp_k$$

- ▶ $\omega(\tau, (p_k)_{k \in \mathcal{P}_{\text{fluid}}})$ is an equation of state for the porous system

Capillary effects

- ▶ Relation between volume fractions and pressures: $\phi_k = -\frac{\partial \omega}{\partial p_k}$
- ▶ Structure of the EoS $\omega(\tau, (p_k)_k)$
 - ▶ Entropy dissipation ($\Psi_{\text{time}} \geq 0$) implies function is **concave**
 - ▶ Rigid matrix implies $\phi = (\text{constant porosity}) = \sum_k -\frac{\partial \omega}{\partial p_k}$
 $\Rightarrow \phi_k(\tau, (p_k + p^0)_k) = \phi_k(\tau, (p_k)_k)$
Volume fractions only depend on relative pressures
- ▶ Capillary pressure curve
 - ▶ Two phases: capillary curve $P_c(\text{Sat})$ and EoS ω are **equivalent**
$$\omega(p_1, p_2) = -\phi \int^{p_1 - p_2} P_c^{-1}(x) dx$$
 - ▶ Three phases and more: capillary curves **not always consistent** with entropy dissipation
 \Rightarrow EoS $\omega(\tau, (p_k)_k)$ generalizes the notion of capillary curve
- ▶ Beyond interface equilibrium: irreversible processes
 \Rightarrow multiple curves: relaxation, hysteresis, ...

Conclusions

- ▶ Thermodynamic framework for flows in porous media
 - ▶ multiphase, compositional, miscible or not
 - ▶ Tractable entropy dissipation
 - ▶ Contains the usual models (Darcy, Fourier, ...), and more
 - ▶ Well posed formulation based on $(\tau, (\nu^i)_i)$
 - ▶ Open for coupling with reactivity

- ▶ Fully thermodynamic explanation of capillary effects
 - ▶ No curvature, no contact angle, ...
 - ▶ Interface equilibrium
 - ▶ Generalization of capillary pressure curve

More information: [Smaï, 2020. *A thermodynamic formulation for multi-phase compositional flows in porous media*] (preprint)