



# Multiphase flow through multilayers of thin porous media: General balance equations and constitutive relationships for a solid–gas–liquid three-phase system

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## ABSTRACT

In this work, we propose a new approach to modeling multiphase flow and solute transport through a stack of thin porous layers. Currently, numerical simulation of thin layers involves discretization across the layer thickness. In our new approach, thin porous layers are treated as a bunch of two-dimensional (2D) interacting continua. Macroscale balance laws are formulated in terms of thickness-averaged material properties. A number of exchange terms are employed to account for exchanges of mass, momentum, energy, and entropy between two neighboring layers. The entropy inequality is then exploited for obtaining constitutive equations to close the problem under study. As an example, simplified governing equations are derived for a system of air–water flow and heat transfer through two thin porous layers. In comparison to previous macroscale models, our model possesses the following distinctive advantages: (1) it is rigorous thermodynamics-based model; (2) it is formulated in terms of layer-thickness-averaged material properties which are usually easily measurable; and (3) it reduces 3D modeling to 2D leading to a very significant reduction of computational efforts.

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## 1. Introduction

Multiphase flow and solute transport through thin layers of porous media are encountered in a number of industrial applications [1–4], such as fuel cells, paper printers, filters, and hygiene products (e.g. diapers and wipes). As an example, consider a polymer electrolyte fuel cell (PEFC), schematically shown in Fig. 1, which has been the subject of extensive studies over the past two decades [5,6,32,33]. A typical PEFC unit consists of gas channels (GCs), gas diffusion layers (GDLs), micro porous layers (MPLs), and catalyst layers (CLs) on both cathode and anode sides. The two sides are connected by a solid polymer electrolyte membrane (PEM). In automotive applications, the GDL, MPL, and CL usually have thicknesses of 150–300 μm, 5–20 μm, and 5–30 μm, respectively. In the in-plane directions, they can have dimensions of around 50 × 50 cm. So, they are very thin layers of porous media stacked upon each other. The operating principles of a PEFC are as follows. Streamed humidified hydrogen (or hydrogen-rich gas) and oxygen (or air) are delivered into the GCs on the anode and cathode sides, respectively. At the anode side, hydrogen diffuses through the diffusion layers and enters into the CL, where each hydrogen molecule splits into two electrons and two protons. The protons

migrate into the cathode CL via the membrane. The electrons cannot enter the membrane and have to travel through an external circuit to the cathode side. There, electrons and oxygen diffuse into the CL where they combine with the protons, which have diffused from the membrane, forming water and generating heat. Though the operating principles are quite simple, several electrochemical and physical processes (e.g. two-phase flow, electrochemical reactions in CL and heat transfer) occur simultaneously. These processes are crucial to the operation of transport PEFCs [7,8]. To increase the performance and durability as well as optimize the material properties for cost reduction, an effective and reliable numerical model for describing water flow and heat transfer in PEFCs is needed. This is the main objective of the present work.

To date, the modeling of flow and transport through such a thin porous medium has been mostly performed in a three-dimensional (3D) discretized domain with many computational cells, based on some macroscale theories like the well-known two-phase Darcy's law [1,9,10]. However, there are a number of problems with this approach. First, currently available macroscale theories are formulated in terms of averaged quantities, which are defined over an average domain known as the representative elementary volume (REV). A major requirement of the REV is that its size must be much larger (10–15 times) than the pore-scale dimensions, but much smaller than the modeling domain size [11]. Obviously, this criterion cannot be satisfied in a thin porous medium. So, the

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## Nomenclature

### Latin symbols

$A^\alpha$	Helmholtz free energy function defined by Eq. (32), ( $L^2/T^2$ )
$\delta A$	cross-sectional area of REV, ( $L^2$ )
$b$	layer thickness, ( $L$ )
$C^\alpha$	mass-specific heat capacity of the $\alpha$ phase, ( $L^2/T^2$ )
$e^\alpha(\rho)$	mass exchange term defined by Eq. (A15), ( $1/T$ )
$e_\alpha^T, e_\alpha^B$	layer-layer mass exchange terms defined by Eqs. (A16) and (A17), ( $L/T$ )
$E^\alpha$	macroscopic internal energy, ( $L^2/T^2$ )
$\mathbf{E}^s$	planar Lagrangian strain tensor, (-)
$\mathbf{F}^s$	solid phase motion
$\mathbf{g}$	gravity vector, ( $L/T^2$ )
$G^\alpha$	Gibbs free energy defined by Eq. (57), ( $L^2/T^2$ )
$h^\alpha$	external heat supply, ( $L^2/T^3$ )
$\mathbf{j}_i$	diffusive flux, ( $M/L^2 T$ )
$\mathbf{j}_{ih}^\alpha$	volume-averaged nonconvective species flux defined by Eq. (B1), ( $M/L^2 T$ )
$J_i^T, J_{i\alpha}^T, J_{i\alpha}^B$	mass transfer into species $i$ in the $\alpha$ phase, ( $1/T$ )
$J_{i\alpha}^T, J_{i\alpha}^B$	layer-layer mass exchanges for species $i$ in the $\alpha$ phase, ( $L/T$ )
$k$	layer index, (-)
$\mathbf{K}$	heat conductivity tensor, ( $M L^2/T^3$ )
$\bar{K}$	energy exchange coefficient between neighboring layers, ( $M/T^3$ )
$l^\alpha$	external supply of entropy, ( $L^2/T^3$ )
$p$	pressure, ( $M/LT^2$ )
$\mathbf{q}$	heat flux, ( $M/T^3$ )
$Q^\alpha$	energy transfer into the $\alpha$ phase, ( $L^2/T^3$ )
$Q_\alpha^T, Q_\alpha^B$	layer-layer energy exchanges defined by Eqs. (B11) and (B12), ( $L^3/T^3$ )
$r_i^\alpha$	mass-averaged chemical reaction rate, ( $1/T$ )
$\mathbf{R}^\alpha$	material property in Eq. (62), ( $1/T$ )
$s$	saturation
$S^\alpha$	macroscopic entropy per unit mass, ( $L^2/T^2$ )
$\delta S_{\alpha\beta}^T$	interfacial area between two phases, ( $L^2$ )
$\delta S_\alpha^T$	interfacial area of the $\alpha$ phase at the top of the layer, ( $L^2$ )

$\delta S_\alpha^B$  interfacial area of the  $\alpha$  phase at the bottom of the layer, ( $L^2$ )

$\mathbf{t}_h^\alpha$  in-plane part of macroscopic stress tensor, ( $M/L T^2$ )

$\mathbf{T}^\alpha$  momentum transfer into the  $\alpha$  phase through phase interfaces, ( $L/T^2$ )

$\mathbf{T}_\alpha^T, \mathbf{T}_\alpha^B$  layer-layer momentum exchanges defined by Eqs. (B7)

and (B8), ( $L^2/T^2$ )

$\mathbf{v}$  velocity vector for bulk phase, ( $L/T$ )

$\mathbf{w}$  velocity vector for interfaces, ( $L/T$ )

### Greek symbols

$\varepsilon$  porosity of porous medium, (-)

$\varepsilon^\alpha$  volume fraction of the  $\alpha$  phase, (-)

$\rho$  mass density, ( $M/L^3$ )

$\psi$  thermodynamic property

$\psi$  microscopic entropy flux; macroscopic entropy flux if with superscript, ( $M/T^3$ )

$\Phi^\alpha$  entropy transfer into the  $\alpha$  phase, ( $L^2/T^3$ )

$\Phi_\alpha^T, \Phi_\alpha^B$  layer-layer entropy exchanges, ( $L^3/T^3$ )

$\Gamma$  entropy production, ( $L^2/T^3$ )

$\Lambda$  total amount of net rate of entropy production, ( $M/T^3$ )

$\theta$  temperature, ( $^\circ$ )

$\omega$  mass fraction, (-)

$\Omega^\alpha$  wettability potential defined by Eq. (61), ( $M/L T^2$ )

$\Pi_m$  material coefficient in Eq. (63), ( $M T^3/L^4$ )

$\Pi_b$  material coefficient in Eq. (64), ( $L^2 T/M$ )

$\Pi_s$  material coefficient in Eq. (65), ( $L T/M$ )

### Superscripts and subscripts

$h$  in-plane part

$\alpha, \beta$  phase indicator

$T$  top of layer

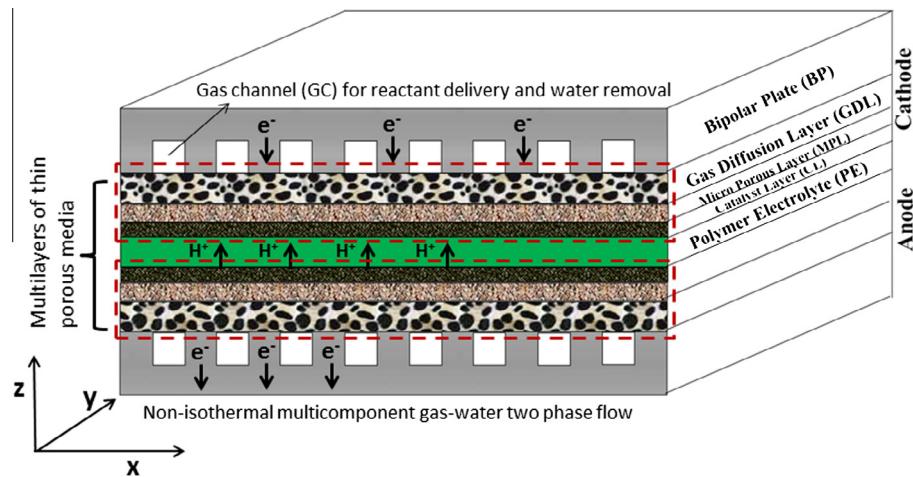
$B$  bottom of layer

$l$  liquid phase

$g$  gas phase

$s$  solid phase

$r$  reference



**Fig. 1.** Schematic of a PEFC unit including gas channels (GCs), gas diffusion layer (GDL), micro porous layer (MPL), catalyst layer (CL) on each side; both sides are connected by a solid polymer electrolyte membrane (PEM). Here, GDL, MPL and CL constitute a system of three thin porous layers. The  $z$  is the through-plane direction, and the  $x$  or  $y$  is the in-plane direction.

application of those macroscale theories to thin porous media (at least in the through-plane direction) is questionable. Second, there are problems with the numerical solution of those macroscale

models. For instance, one needs to discretize a thin porous medium into computational cells, whose size may be comparable to the pore sizes. This suggests that the methods are not applicable to

such thin domains. Furthermore, the interfacial conditions between adjacent layers, needed in numerical methods, are usually not well defined. Most importantly, 3D numerical modeling of a number of interacting thin porous layers often requires heavy computational efforts [1]. This may be the major reason why the stack-level modeling of fuel cells has not been performed until now. Third, the numerical modeling needs parameter values to be specified for each computational cell in the through-plane direction. But, such a detailed and high-resolution distribution of material properties is usually unavailable. Instead, we commonly know effective properties averaged over the layer thickness of a thin medium.

Therefore, in this work we propose a new approach, to model a system of multilayers of thin porous media as 2D interacting continua. We develop the governing equations of multiphase multicomponent flow in terms of thickness-averaged material properties. The exchange of thermodynamic properties (e.g. mass, momentum, and energy) between adjacent layers is also described in terms of thickness-averaged quantities. This means that in modeling, we only need to discretize the layers in the planar (i.e. in-plane) directions which will lead to a very significant reduction of computational efforts.

For deriving the thickness-averaged macroscale governing equations, we employ the averaging-thermodynamic approach for multiphase flow in porous media developed by Hassanizadeh and Gray [12–14]. In this approach, conservation laws at the microscale are averaged over an REV to obtain macroscopic conservation equations. No assumptions are made about constitutive relationships at the microscale. Instead, constitutive assumptions are introduced at the macroscale either by direct postulation of desirable relations or by following the Coleman and Noll method for the exploitation of entropy inequality [15]. Although this method is more general than other approaches [16,17], the ultimate generality of obtained results depends on the degree of complexity of the constitutive assumptions postulated. Furthermore, functional dependence of some exchange variables must be determined from experimental investigations.

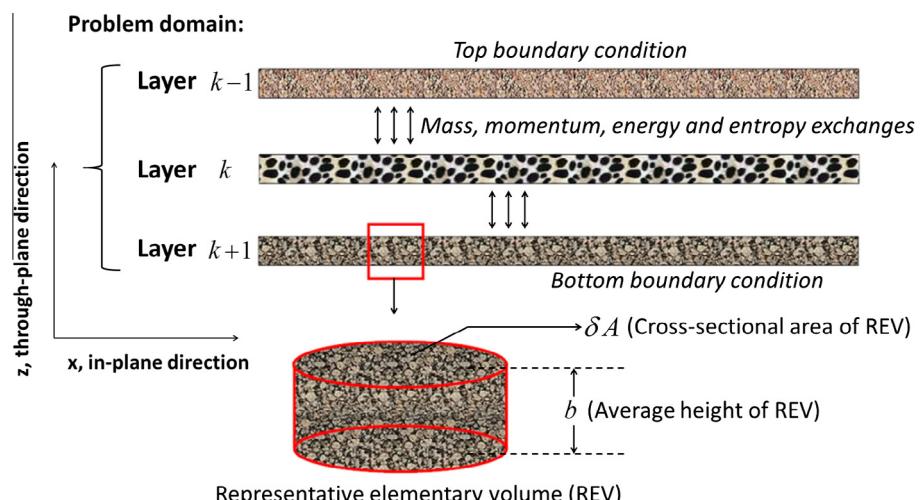
Vertically-averaged conservation equations for multiphase flow in a single porous layer were developed by Gray [18]. He also developed constitutive equations for slow two-phase flow in a geothermal reservoir [19] based on the Coleman and Noll method of exploitation of the entropy inequality. Hassanizadeh [20,21] derived the single-phase Darcy's law and Fickian dispersion equation for multicomponent saturated flow. By including the

thermodynamic description of the surfaces separating phases at the microscale, Hassanizadeh and Gray [22,23] derived an extended form of Darcy's law for multiphase flow in porous media. They proposed that including a dependence of the macroscale capillary pressure on the fluid–fluid interfacial area may provide a quantitative description of capillary hysteresis. Reggiani et al. [24] formulated rigorous conservation equations for mass, momentum, energy, and entropy for a watershed organized around a channel network. In order to close the problem under study, they developed constitutive equations for specific types of watersheds by exploiting the second law of thermodynamics [25].

The specific goals of this research are to: (1) formulate 2D thickness-averaged governing equations for multiphase multicomponent flow through multilayers of thin porous media; (2) derive constitutive relationships for a system of two thin porous layers made of one solid and two fluid phases. The paper is organized as follows. First, we briefly introduce the average approach used in this work. Then, kinematics, auxiliary relations, and notation are given. A detailed derivation of 2D balance laws is presented along with restrictions on the exchange terms at the microscale phase interfaces and layer–layer boundaries. Furthermore, the macroscopic form of the second law of thermodynamics will be introduced which serves to restrict our constitutive assumptions for multiphase flow through thin porous layers. In Section 7, we explore the entropy inequality for a system of two layers of thin porous media with solid, gas, and liquid as the three phases. The linearization theory is used to obtain simplified constitutive equations. As a demonstration, in Section 8, the simplified governing equations for air–water two-phase flow and heat transfer within two thin porous layers are presented. At the end, a discussion of the results and conclusions are provided.

## 2. Averaging approach

In this work, we consider the problem of multiphase multicomponent flow through multilayers of thin porous media which are assumed to be stacked with no gap between them. A schematic representation of the through-plane cross section of the system showing layers  $k-1$ ,  $k$ , and  $k+1$  is given in Fig. 2. Although in this illustration the layers are shown to have a constant thickness, in general their thickness may change in the planar directions. We assign an averaging volume (REV) to each layer (see the lower graph in Fig. 2). The cross-sectional area of REV,  $\delta A$ , is assumed to be the same for all layers and constant in the planar directions. At any



**Fig. 2.** Schematic representation of three thin porous layers, which may exchange mass, momentum, and energy. Also, a typical averaging domain (REV) is shown. Note that the layer thickness and thus the REV height can be spatially variable. Also, in reality, the layers are tightly stacked and there is no gap between them.

given point, the height of REV,  $b$ , is equal to the layer thickness. By moving the centroid of REV along a layer, a continuous 2D field of average quantities will be obtained for the layer. By averaging thermodynamic quantities over the proposed REV, it is obvious that in each thin porous medium, we average out the through-plane distribution of quantities, and only the in-plane distribution is kept. In this approach, each layer of thin porous medium is modeled as a 2D continuum with corresponding planar balance equations which will be derived in Section 4. Also, equations will be developed for the exchange of thermodynamic properties (mass, momentum, energy, and entropy) between adjacent layers via layer–layer boundaries. At the end, proper boundary conditions need to be supplemented for the top surface of the first layer and the bottom surface of the last layer.

### 3. Kinematics, auxiliary relations and notation

Macroscopic quantities are defined at the scale of an REV with volume,  $\delta V = b\delta A$ . Throughout this work, all introduced quantities with a phase indicator in the superscript or subscript are macro-scale. Any averaged thermodynamic quantity  $\langle f \rangle_\alpha$  only depends on the planar directions. For instance,  $\rho^\alpha$  is the ratio of mass to volume of the  $\alpha$  phase present within an REV. Because we average out the through-plane distribution of quantities, as a consequence, only the in-plane components of some vectorial and tensorial variables appear in the derived 2D macroscale balance laws. Throughout this work, we use the subscript  $h$  to denote planar components of a vector or tensor. For instance, in Cartesian coordinate, the planar velocity vector,  $\mathbf{v}_h^\alpha$ , is equal to  $\{v_x^\alpha, v_y^\alpha\}$ . Similarly, the planar part of stress tensor,  $\mathbf{t}_h^\alpha$ , is given as:

$$\mathbf{t}_h^\alpha = \begin{Bmatrix} t_{xx}^\alpha, t_{xy}^\alpha, t_{xz}^\alpha \\ t_{yx}^\alpha, t_{yy}^\alpha, t_{yz}^\alpha \end{Bmatrix} \quad (1)$$

Also, we have the planar spatial gradient,  $\nabla_h$ , with components  $\{\partial/\partial x, \partial/\partial y\}$ .

When modeling a multiphase system, it is convenient to employ the notions of volume fraction,  $\varepsilon^\alpha$ , and saturation,  $s^\alpha$ . For a solid–gas–liquid three-phase system, we have:

$$s^\alpha = \varepsilon^\alpha / \varepsilon \quad \alpha = g, l \quad (2)$$

such that

$$s^g + s^l = 1 \quad (3a)$$

$$\varepsilon^s = 1 - \varepsilon \quad (3b)$$

where the superscripts  $g$ ,  $l$ , and  $s$  denote the gas, liquid, and solid phases, respectively, and  $\varepsilon$  is the porosity.

Motion of solid phase is defined as a transformation  $\mathbf{F}^s(\mathbf{X}, t)$  which changes the reference configuration  $\mathbf{X}$  of the solid at time  $t = 0$  to a new configuration  $\mathbf{x}$  at time  $t$ , such that:

$$\mathbf{x} = \mathbf{F}^s(\mathbf{X}, t) \quad (4)$$

It is worth noting that in this work, we will employ  $\mathbf{F}_h^s$  to describe the planar motion of solid phase, while its through-plane motion is tracked by the changes in the layer thickness,  $b$ . So, the planar Lagrangian strain tensor  $\mathbf{E}^s$  ( $2 \times 2$ ) is defined by:

$$\mathbf{E}^s = \frac{1}{2} \left[ (\text{GRAD} \mathbf{F}_h^s) \cdot (\text{GRAD} \mathbf{F}_h^s)^T - \mathbf{I} \right] \quad (5)$$

where  $\text{GRAD}$  is the planar gradient operation with respect to the reference configuration, and  $\mathbf{I}$  is the planar identity tensor ( $2 \times 2$ ).

In multiphase mechanics, the absolute velocities of phases are not representative of any mechanical changes. Therefore, we introduce the auxiliary variables, relative velocity and relative temperature:

$$\mathbf{v}^{\alpha,r} = \mathbf{v}^\alpha - \mathbf{v}^r \quad (6a)$$

$$\theta^{\alpha,r} = \theta^\alpha - \theta^r \quad (6b)$$

where  $\mathbf{v}^r$  and  $\theta^r$  are some reference velocity and temperature, respectively. Throughout this paper, a comma in the superscripts will indicate relative variables.

In formulating balance laws and the second law of thermodynamics, it is more convenient to work with total material derivatives instead of partial derivatives. The material derivative of a function  $\psi$ , is introduced as:

$$\frac{D_h^\alpha \psi}{Dt} = \frac{\partial \psi}{\partial t} + \mathbf{v}_h^\alpha \cdot \nabla_h \psi \quad (7)$$

This equation may be written in terms of the material derivative with respect to a reference velocity  $\mathbf{v}^r$ :

$$\frac{D_h^\alpha \psi}{Dt} = \frac{D_h^r \psi}{Dt} + \mathbf{v}_h^{\alpha,r} \cdot \nabla_h \psi \quad (8)$$

The planar deformation rate tensor,  $d^\alpha$  ( $2 \times 2$ ), is defined by:

$$d^\alpha = \frac{1}{2} \left[ \nabla_h \mathbf{v}_h^\alpha + (\nabla_h \mathbf{v}_h^\alpha)^T \right] \quad (9)$$

Finally, we introduce the used convention in the layer index throughout the work. A general thin porous layer is denoted by layer  $k$ . When multilayers are in consideration, layer  $k - 1$  denotes the layer on the top of layer  $k$ , and layer  $k + 1$  is the layer on the bottom of layer  $k$ . When the layer index is omitted, it means that the referred variables or equations hold for each layer.

### 4. Balance laws

For fully describing thermodynamic processes in a multiphase flow system, two sets of macroscopic conservation equations are necessary: one set in terms of average phase properties and the other set in terms of average interfacial properties. The two sets of equations are coupled via terms accounting for exchange of thermodynamic properties between phase and interface continua [22]. However, in order to reduce the algebra and as a first approximation, we assume that phase interfaces and layer–layer boundaries do not store any thermodynamic properties. In this section, we will provide macroscale balance equations for mass, momentum, chemical species, energy, and entropy of the  $\alpha$  phase in a typical layer  $k$ . Details of derivation of the macroscale general balance law, based on the average of the general form of a microscale balance equation (Eq. (A1)), and the definition of macroscale thermodynamic quantities are presented in Appendix A. The variables that should go into Eq. (A1) in order to obtain specific balance equations are listed in Table 1. The average of Eq. (A1) is shown to be Eq. (A13). In the remainder of this section, we will introduce specific REV-scale balance laws.

#### 4.1. Mass balance

Eq. (A13) gives the REV-scale balance equation for a typical thermodynamic property of the  $\alpha$  phase,  $\psi$ . According to Table 1, when  $\psi = 1$ ,  $\mathbf{i} = 0$ ,  $\gamma = 0$ , and  $G = 0$ , the macroscale mass balance equation for the  $\alpha$  phase in layer  $k$  can be given as:

$$\begin{aligned} \frac{\partial}{\partial t} (b \varepsilon^\alpha \rho^\alpha) \Big|_k + \nabla_h \cdot (b \varepsilon^\alpha \rho^\alpha \mathbf{v}_h^\alpha) \Big|_k - b \varepsilon^\alpha \rho^\alpha e^\alpha(\rho) \Big|_k \\ = \varepsilon^\alpha \rho^\alpha (e_\alpha^T + e_\alpha^B) \Big|_k \end{aligned} \quad (10)$$

where the vertical bar with subscript  $k$  indicates that the term preceding the bar belongs to layer  $k$ ,  $b$  is the layer thickness,  $\varepsilon^\alpha$  is the volume fraction of the  $\alpha$  phase,  $\rho^\alpha$  is the phase density,  $\mathbf{v}_h^\alpha$  is the 2D in-plane velocity vector,  $e^\alpha(\rho)$  [ $1/T$ ] is the mass exchange

**Table 1**

Microscopic quantities used in the general transport Eq. (A1) for obtaining specific balance laws.

Quantity	$\psi$	$\mathbf{i}$	$f$	$G$
Mass	1	0	0	0
Chemical component	$\omega_i$ , Mass fraction	$\mathbf{j}_h$ , Diffusive flux	0	$r_i$ , Reaction rate
Linear momentum	$\mathbf{v}$ , Momentum per unit mass	$\mathbf{t}$ , Stress	$\mathbf{g}$ , gravity	0
Energy	$E + 1/2 v^2$ , Internal and kinetic energy per unit mass	$\mathbf{t} \cdot \mathbf{v} + \mathbf{q}$ , Energy flux	$\mathbf{g} \cdot \mathbf{v} + h$	0
Entropy	$S$ , Entropy per unit mass	$\psi$	$l$	$\Gamma$ , Rate of entropy production

between the  $\alpha$  phase and all other phases within the layer,  $e_\alpha^T$  [L/T] is the  $\alpha$ -phase mass exchange with layer  $k - 1$ , and  $e_\alpha^B$  [L/T] is the  $\alpha$ -phase mass exchange with layer  $k + 1$ . Note that the velocity vector and the gradient vector have in-plane components only.

For later use, we recast Eq. (10) in terms of the material derivative:

$$\begin{aligned} \frac{D_h}{Dt} (b\epsilon^\alpha \rho^\alpha) \Big|_k + b\epsilon^\alpha \rho^\alpha \nabla_h \cdot \mathbf{v}_h^\alpha \Big|_k - b\epsilon^\alpha \rho^\alpha e^\alpha(\rho) \Big|_k \\ = \epsilon^\alpha \rho^\alpha (e_\alpha^T + e_\alpha^B) \Big|_k \end{aligned} \quad (11)$$

#### 4.2. Species mass balance

For the sake of neatness, in what follows, we drop the layer index  $k$  at the end of each term. But, we would recover it whenever confusion may arise. For a component  $i$  of the  $\alpha$  phase, with mass fraction  $\omega_i$ , its mass conservation equation is:

$$\begin{aligned} \frac{\partial}{\partial t} (b\epsilon^\alpha \rho^\alpha \omega_i^\alpha) + \nabla_h \cdot (b\epsilon^\alpha \rho^\alpha \mathbf{v}_h^\alpha \omega_i^\alpha) - \nabla_h \cdot (b\mathbf{j}_{ih}^\alpha) \\ - b\epsilon^\alpha \rho^\alpha [\omega_i^\alpha e^\alpha(\rho) + J_i^\alpha] \\ = b\epsilon^\alpha \rho^\alpha r_i^\alpha + \epsilon^\alpha \rho^\alpha \left[ (\omega_i^\alpha e_\alpha^T + J_{i\alpha}^T) + (\omega_i^\alpha e_\alpha^B + J_{i\alpha}^B) \right] \end{aligned} \quad (12)$$

where  $\mathbf{j}_{ih}^\alpha$  (M/L<sup>2</sup>T) is the volume-averaged nonconvective species flux (defined in Appendix B) composed of two parts: the averaged diffusive flux and the dispersion part which depends on the fluctuations of both velocity and mass fraction. We note that,  $\langle \mathbf{j} \rangle_\alpha$  and  $\langle \rho \mathbf{v} \omega_i \rangle_\alpha$  (Eq. (B1)) are the vectorial quantities with three components in the Cartesian coordinate. For species transport inside the layer, we only take the in-plane components because of no through-plane gradient at the macroscale. But, the through-plane part may affect the mass exchange of species between layers. The mass exchange of species with adjacent layers is taken into account by the terms inside the bracket on the r.h.s of Eq. (12).  $J_i^\alpha$  (1/T) is the diffusive transfer of species  $i$  into the  $\alpha$  phase in addition to the mass transfer caused by phase change,  $\omega_i^\alpha e^\alpha(\rho)$ .  $r_i^\alpha$  (1/T) is the mass-averaged chemical reaction rate. With the help of the continuity equation (Eq. (11)), we can rewrite Eq. (12) in terms of the material derivative:

$$\begin{aligned} b\epsilon^\alpha \rho^\alpha \frac{D_h \omega_i^\alpha}{Dt} - \nabla_h \cdot (b\mathbf{j}_{ih}^\alpha) - b\epsilon^\alpha \rho^\alpha J_i^\alpha \\ = b\epsilon^\alpha \rho^\alpha r_i^\alpha + \epsilon^\alpha \rho^\alpha (J_{i\alpha}^T + J_{i\alpha}^B) \end{aligned} \quad (13)$$

#### 4.3. Momentum balance

The conservation equation for the momentum per unit mass,  $\mathbf{v}^\alpha$  (L/T), is given as:

$$\begin{aligned} \frac{\partial}{\partial t} (b\epsilon^\alpha \rho^\alpha \mathbf{v}^\alpha) + \nabla_h \cdot (b\epsilon^\alpha \rho^\alpha \mathbf{v}_h^\alpha \mathbf{v}^\alpha) - \nabla_h \cdot (b\mathbf{t}_h^\alpha) - b\epsilon^\alpha \rho^\alpha \mathbf{g}^\alpha \\ - b\epsilon^\alpha \rho^\alpha [\mathbf{v}^\alpha e^\alpha(\rho) + \mathbf{T}^\alpha] = \epsilon^\alpha \rho^\alpha \left[ (\mathbf{v}^\alpha e_\alpha^T + \mathbf{T}_\alpha^T) + (\mathbf{v}^\alpha e_\alpha^B + \mathbf{T}_\alpha^B) \right] \end{aligned} \quad (14)$$

Here,  $\mathbf{t}_h^\alpha$  (M/L T<sup>2</sup>) is the in-plane macroscopic stress tensor. It is a mixed 2 × 3 tensor (defined in Appendix B).  $\mathbf{v}^\alpha e^\alpha(\rho)$  accounts for the momentum carried by the mass involved in the mass exchange, and  $\mathbf{T}^\alpha$  [L/T<sup>2</sup>] is the momentum exchange between the  $\alpha$  phase and all other phases. The momentum exchange with the upper and lower layers is accounted for by the terms on the r.h.s of Eq. (14). Note that the macroscopic momentum equation (Eq. (14)) has components in all three directions; i.e. not only the in-plane but also the through-plane directions. Again, with the help of the continuity equation, Eq. (14) can be reduced to the following form:

$$\begin{aligned} b\epsilon^\alpha \rho^\alpha \frac{D_h \mathbf{v}^\alpha}{Dt} - \nabla_h \cdot (b\mathbf{t}_h^\alpha) - b\epsilon^\alpha \rho^\alpha \mathbf{g}^\alpha - b\epsilon^\alpha \rho^\alpha \mathbf{T}^\alpha \\ = \epsilon^\alpha \rho^\alpha (\mathbf{T}_\alpha^T + \mathbf{T}_\alpha^B) \end{aligned} \quad (15)$$

#### 4.4. Energy balance

The macroscale energy balance equation reads:

$$\begin{aligned} \frac{\partial}{\partial t} \left\{ b\epsilon^\alpha \rho^\alpha \left[ E^\alpha + \frac{1}{2} (\mathbf{v}^\alpha)^2 \right] \right\} + \nabla_h \cdot \left\{ b\epsilon^\alpha \rho^\alpha \mathbf{v}_h^\alpha \left[ E^\alpha + \frac{1}{2} (\mathbf{v}^\alpha)^2 \right] \right\} \\ - \nabla_h \cdot (b\mathbf{t}_h^\alpha \cdot \mathbf{v}^\alpha) - \nabla_h \cdot (b\mathbf{q}_h^\alpha) - b\epsilon^\alpha \rho^\alpha \mathbf{g}^\alpha \cdot \mathbf{v}^\alpha - b\epsilon^\alpha \rho^\alpha h^\alpha \\ - b\epsilon^\alpha \rho^\alpha \left\{ \left[ E^\alpha + \frac{1}{2} (\mathbf{v}^\alpha)^2 \right] e^\alpha(\rho) + Q^\alpha + \mathbf{T}^\alpha \cdot \mathbf{v}^\alpha \right\} \\ = \epsilon^\alpha \rho^\alpha \left\{ \left[ E^\alpha + \frac{1}{2} (\mathbf{v}^\alpha)^2 \right] (e_\alpha^T + e_\alpha^B) + Q_\alpha^T + Q_\alpha^B + \mathbf{T}_\alpha^T \cdot \mathbf{v}^\alpha + \mathbf{T}_\alpha^B \cdot \mathbf{v}^\alpha \right\} \end{aligned} \quad (16)$$

Here,  $E^\alpha$  (L<sup>2</sup>/T<sup>2</sup>) is the macroscopic internal energy that includes the average of microscale deviatoric kinetic energy,  $(\tilde{v}^2/2)^\alpha$  [13],  $\mathbf{q}_h^\alpha$  (M/T<sup>3</sup>) is the macroscopic heat flux,  $h^\alpha$  (L<sup>2</sup>/T<sup>3</sup>) is the macroscopic external energy source,  $Q^\alpha$  (L<sup>2</sup>/T<sup>3</sup>) is the heat exchange between the  $\alpha$  phase and all other phases inside the layer,  $Q_\alpha^T$  and  $Q_\alpha^B$  (L<sup>3</sup>/T<sup>3</sup>) are the heat exchanges with the upper and lower layers, respectively. With the help of the continuity and momentum equations, Eq. (16) can be reduced to the following form:

$$\begin{aligned} b\epsilon^\alpha \rho^\alpha \frac{D_h E^\alpha}{Dt} - b\mathbf{t}_h^\alpha : \nabla_h \mathbf{v}^\alpha - \nabla_h \cdot (b\mathbf{q}_h^\alpha) - b\epsilon^\alpha \rho^\alpha h^\alpha - b\epsilon^\alpha \rho^\alpha Q^\alpha \\ = \epsilon^\alpha \rho^\alpha (Q_\alpha^T + Q_\alpha^B) \end{aligned} \quad (17)$$

where the colon sign in the second term on the l.h.s. denotes a double inner product operation.

#### 4.5. Entropy balance

Finally, the macroscale entropy balance equation reads:

$$\begin{aligned} \frac{\partial}{\partial t} (b\epsilon^\alpha \rho^\alpha S^\alpha) + \nabla_h \cdot (b\epsilon^\alpha \rho^\alpha \mathbf{v}_h^\alpha S^\alpha) - \nabla_h \cdot (b\psi_h^\alpha) - b\epsilon^\alpha \rho^\alpha l^\alpha \\ - b\epsilon^\alpha \rho^\alpha [S^\alpha e^\alpha(\rho) + \Phi^\alpha] \\ = b\epsilon^\alpha \rho^\alpha \Gamma^\alpha + \epsilon^\alpha \rho^\alpha \left[ (S^\alpha e_\alpha^T + \Phi_\alpha^T) + (S^\alpha e_\alpha^B + \Phi_\alpha^B) \right] \end{aligned} \quad (18)$$

Here,  $S^x$  ( $L^2/T^2$ ) is the macroscale internal entropy per unit mass,  $\psi_h^x$  ( $M/T^3$ ) (Eq. (B13)) is the entropy flux vector,  $l^x$  ( $L^2/T^3$ ) is the external supply of entropy, and  $\Gamma^x$  ( $L^2/T^3$ ) is the rate of net production of entropy. With the help of the continuity equation, Eq. (18) can be rewritten in the form of material description:

$$b\varepsilon^x \rho^x \frac{D_h^x S^x}{Dt} - \nabla_h \cdot (b\psi_h^x) - b\varepsilon^x \rho^x l^x - b\varepsilon^x \rho^x \Phi^x = b\varepsilon^x \rho^x \Gamma^x + \varepsilon^x \rho^x (\Phi_x^T + \Phi_x^B) \quad (19)$$

## 5. Restrictions on the exchange terms

As mentioned earlier, thermodynamic quantities are exchanged among phases within a layer, as well as between adjacent layers via layer-layer boundaries. Also as explained before, we assume that there are no thermodynamic properties associated with phase interfaces or layer-layer boundaries. This means that they are not able to store any properties or sustain stress. Thus, standard microscale continuity equations (i.e. conservative restrictions for the balance equations) can be applied at these interfaces, as initially derived by Eringen [30]. The averaging of these conditions across phase interfaces results in the following macroscale restrictions within each and every layer (see Appendix A for details):

$$\sum_x b\varepsilon^x \rho^x e^x(\rho) = 0 \quad (20)$$

$$\sum_x b\varepsilon^x \rho^x [\omega_i^x e^x(\rho) + J_i^x] = 0 \quad (21)$$

$$\sum_x b\varepsilon^x \rho^x [\mathbf{v}^x e^x(\rho) + \mathbf{T}^x] = 0 \quad (22)$$

$$\sum_x b\varepsilon^x \rho^x \left\{ \left[ E^x + \frac{1}{2} (\nu^x)^2 \right] e^x(\rho) + Q^x + \mathbf{T}^x \cdot \mathbf{v}^x \right\} = 0 \quad (23)$$

$$\sum_x b\varepsilon^x \rho^x [S^x e^x(\rho) + \Phi^x] = 0 \quad (24)$$

Here, Eqs. (20)–(24) state the constraints on the exchanges of mass, chemical species, momentum, energy, and entropy, respectively. These restrictions can provide guidelines in selecting constitutive relationships, so that the global conservation principles are not violated.

The averaging of continuity conditions for the exchange of thermodynamic properties between layers results in the following macroscale restrictions across two neighboring layers (for instance, layer  $k$  and layer  $k+1$ ). For the time being, to simplify the problem, we assume no phase change happening just at the layer-layer boundaries. In other words, the exchanges of thermodynamic quantities occur only inside the respective phases, which can be given as follows:

$$(\varepsilon^x \rho^x e_x^B)|_k + (\varepsilon^x \rho^x e_x^T)|_{k+1} = 0 \quad (25)$$

$$[\varepsilon^x \rho^x (\omega_i^x e_x^B + J_x^B)]|_k + [\varepsilon^x \rho^x (\omega_i^x e_x^T + J_x^T)]|_{k+1} = 0 \quad (26)$$

$$[\varepsilon^x \rho^x (\mathbf{v}^x e_x^B + \mathbf{T}_x^B)]|_k + [\varepsilon^x \rho^x (\mathbf{v}^x e_x^T + \mathbf{T}_x^T)]|_{k+1} = 0 \quad (27)$$

$$\left\{ \varepsilon^x \rho^x \left\{ \left[ E^x + \frac{1}{2} (\nu^x)^2 \right] e_x^B + Q_x^B + \mathbf{T}_x^B \cdot \mathbf{v}^x \right\} \right\}|_k + \left\{ \varepsilon^x \rho^x \left\{ \left[ E^x + \frac{1}{2} (\nu^x)^2 \right] e_x^T + Q_x^T + \mathbf{T}_x^T \cdot \mathbf{v}^x \right\} \right\}|_{k+1} = 0 \quad (28)$$

$$[\varepsilon^x \rho^x (S^x e_x^B + \Phi_x^B)]|_k + [\varepsilon^x \rho^x (S^x e_x^T + \Phi_x^T)]|_{k+1} = 0 \quad (29)$$

Here, Eqs. (25)–(29) respectively state the macroscale conservative restrictions between the bottom of layer  $k$  and the top of layer  $k+1$ , for the exchanges of mass, chemical species, momentum, energy, and entropy.

## 6. The second law of thermodynamics

The second law of thermodynamics dictates the sign of net entropy production of the system of interest. According to this law, regardless of what the prevailing processes are, the rate of net production of entropy of the whole system must be non-negative. For a system of  $N$  layers of thin porous media, the total rate of net entropy production and the second law should be written as:

$$\Lambda = \sum_{k=1}^N \sum_x b\varepsilon^x \rho^x \Gamma^x \Big|_k \geq 0 \quad (30)$$

Using the entropy balance (Eq. (19)), we can recast the second law into the following form:

$$\begin{aligned} \Lambda = \sum_{k=1}^N \sum_x b\varepsilon^x \rho^x \Gamma^x \Big|_k &= \sum_{k=1}^N \sum_x b\varepsilon^x \rho^x \frac{D_h^x S^x}{Dt} \Big|_k - \sum_{k=1}^N \sum_x \nabla_h \cdot (b\psi_h^x) \Big|_k \\ &- \sum_{k=1}^N \sum_x b\varepsilon^x \rho^x l^x \Big|_k - \sum_{k=1}^N \sum_x b\varepsilon^x \rho^x \Phi^x \Big|_k - \sum_{k=1}^N \sum_x \varepsilon^x \rho^x (\Phi_x^T + \Phi_x^B) \Big|_k \\ &\geq 0 \end{aligned} \quad (31)$$

In developing constitutive equations, it is convenient to employ Helmholtz free energy function instead of internal energy. The  $\alpha$ -phase Helmholtz free energy,  $A^x$ , is defined by:

$$A^x = E^x - \theta^x S^x \quad (32)$$

where  $\theta^x$  is the macroscopic absolute temperature function, which is always positive.

Division of the energy balance equation (Eq. (17)) by  $\theta^x$ , subtracting it from inequality (31), and subsequent use of Eq. (32) yield the following form of entropy balance equation:

$$\begin{aligned} \Lambda = \sum_{k=1}^N \sum_x b\varepsilon^x \rho^x \Gamma^x \Big|_k &= - \sum_{k=1}^N \sum_x \frac{b\varepsilon^x \rho^x}{\theta^x} \left( \frac{D_h^x A^x}{Dt} + S^x \frac{D_h^x \theta^x}{Dt} \right) \Big|_k \\ &+ \sum_{k=1}^N \sum_x \frac{b}{\theta^x} \mathbf{t}_h^x : \nabla_h \mathbf{v}^x \Big|_k \\ &+ \sum_{k=1}^N \sum_x \left[ \frac{1}{\theta^x} \nabla_h \cdot (b\mathbf{q}_h^x) - \nabla_h \cdot (b\psi_h^x) \right] \Big|_k \\ &+ \sum_{k=1}^N \sum_x \left( \frac{1}{\theta^x} b\varepsilon^x \rho^x h^x - b\varepsilon^x \rho^x l^x \right) \Big|_k \\ &+ \sum_{k=1}^N \sum_x \frac{b\varepsilon^x \rho^x}{\theta^x} Q^x \Big|_k - \sum_{k=1}^N \sum_x b\varepsilon^x \rho^x \Phi^x \Big|_k \\ &+ \sum_{k=1}^N \sum_x \frac{\varepsilon^x \rho^x}{\theta^x} (Q_x^T + Q_x^B) \Big|_k \\ &- \sum_{k=1}^N \sum_x \varepsilon^x \rho^x (\Phi_x^T + \Phi_x^B) \Big|_k \geq 0 \end{aligned} \quad (33)$$

Next, we use the definitions given by Eqs. (6)–(8) and the phase-interface constraints Eqs. (20) and (22)–(24), to rewrite the entropy inequality in terms of reference material derivative, relative velocity and relative temperature. After some manipulation and algebra, we obtain the following entropy inequality:

$$\begin{aligned}
\Lambda = \sum_{k=1}^N \sum_{\alpha} b \varepsilon^{\alpha} \rho^{\alpha} \Gamma^{\alpha} \Big|_k &= - \sum_{k=1}^N \sum_{\alpha} \frac{b \varepsilon^{\alpha} \rho^{\alpha}}{\theta^{\alpha}} \left( \frac{D_h^r A^{\alpha}}{Dt} + S^{\alpha} \frac{D_h^r \theta^{\alpha}}{Dt} + \mathbf{v}_h^{\alpha,r} \cdot \nabla_h A^{\alpha} \right. \\
&\quad \left. + S^{\alpha} \mathbf{v}_h^{\alpha,r} \cdot \nabla_h \theta^{\alpha} \right) \Big|_k + \sum_{k=1}^N \sum_{\alpha} \frac{b}{\theta^{\alpha}} \mathbf{t}_h^{\alpha} : \nabla_h \mathbf{v}^{\alpha} \Big|_k \\
&+ \sum_{k=1}^N \sum_{\alpha} \left[ \frac{1}{\theta^{\alpha}} \nabla_h \cdot (b \mathbf{q}_h^{\alpha}) - \nabla_h \cdot (b \psi_h^{\alpha}) \right] \Big|_k \\
&+ \sum_{k=1}^N \sum_{\alpha} \left( \frac{1}{\theta^{\alpha}} b \varepsilon^{\alpha} \rho^{\alpha} h^{\alpha} - b \varepsilon^{\alpha} \rho^{\alpha} l^{\alpha} \right) \Big|_k - \sum_{k=1}^N \sum_{\alpha} \frac{b \varepsilon^{\alpha} \rho^{\alpha}}{\theta^{\alpha}} e^{\alpha}(\rho) A^{\alpha} \Big|_k \\
&- \sum_{k=1}^N \sum_{\alpha} \frac{b \varepsilon^{\alpha} \rho^{\alpha} \theta^{\alpha,r}}{\theta^{\alpha} \theta^r} [e^{\alpha}(\rho) E^{\alpha} + Q^{\alpha}] \Big|_k \\
&- \sum_{k=1}^N \sum_{\alpha} \frac{b \varepsilon^{\alpha} \rho^{\alpha}}{\theta^r} \left[ \frac{1}{2} (\mathbf{v}^{\alpha,r})^2 e^{\alpha}(\rho) + \mathbf{T}^{\alpha} \cdot \mathbf{v}^{\alpha,r} \right] \Big|_k \\
&+ \sum_{k=1}^N \sum_{\alpha} \frac{\varepsilon^{\alpha} \rho^{\alpha}}{\theta^{\alpha}} (Q_{\alpha}^T + Q_{\alpha}^B) \Big|_k - \sum_{k=1}^N \sum_{\alpha} \varepsilon^{\alpha} \rho^{\alpha} (\Phi_{\alpha}^T + \Phi_{\alpha}^B) \Big|_k \geq 0 \quad (34)
\end{aligned}$$

This is the macroscopic form of the second law of thermodynamics which serves to restrict the behaviors of multiphase flow through multilayers of thin porous media.

## 7. Constitutive equations for two-phase flow and heat transfer in thin porous media layers

### 7.1. Assumptions for two-phase flow in a system of two thin porous layers

The balance laws developed above are for a thin porous medium which belongs to a stack of many thin layers. They account for nonequilibrium heat and mass transfer among phases within a layer as well as between adjacent layers. In this section, we consider a system of two thin porous layers as shown in Fig. 3. At this stage, we do not include transport of any chemical species in order to limit the complexity of equations. We develop constitutive equations for solid, gas, and liquid phases by exploring the second law of thermodynamics. In particular, our focus will be on the equations of motion of the two fluids inside each layer, and the exchanges of mass and energy between the two layers.

To further simplify the system under study, we make the following main assumptions:

- First, there are no phase changes. This means that intraphase mass exchange terms are zero:

$$e^{\alpha}(\rho) = 0 \quad (35)$$

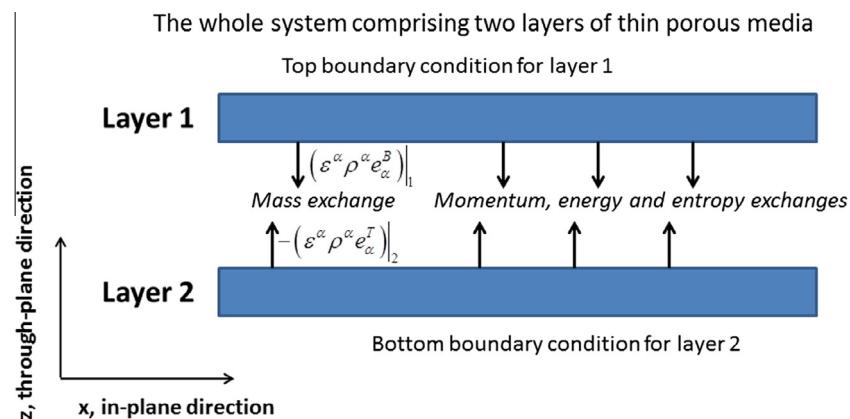


Fig. 3. Schematic graph of a system of two thin porous layers. The exchange of thermodynamic properties occurs at the layer–layer boundary. Boundary conditions are imposed at the top of the first layer and the bottom of the second layer.

Note that we still allow for the exchange of mass of a given phase between two neighboring layers. But, the restrictions Eqs. (25) and (27)–(29) apply to the layer–layer exchange terms.

• Next, we assume that local thermal equilibrium prevails among phases within each layer. In other words, locally all phases within a layer share the same temperature  $\theta_k$ :

$$\theta^{\alpha}|_k = \theta_k \quad (36)$$

where  $\theta_k$  is the macroscopic temperature of layer  $k$ .

Due to the assumption of local thermal equilibrium, we only need one energy equation for each layer. This is obtained by summing energy equations of all phases of a given layer:

$$\begin{aligned}
\sum_{\alpha} b \varepsilon^{\alpha} \rho^{\alpha} \frac{D_h^{\alpha} E^{\alpha}}{Dt} - \sum_{\alpha} b \mathbf{t}_h^{\alpha} : \nabla_h \mathbf{v}^{\alpha} - \sum_{\alpha} \nabla_h \cdot (b \mathbf{q}_h^{\alpha}) - \rho h \\
- \sum_{\alpha} b \varepsilon^{\alpha} \rho^{\alpha} Q^{\alpha} \\
= \sum_{\alpha} \varepsilon^{\alpha} \rho^{\alpha} (Q_{\alpha}^T + Q_{\alpha}^B) \quad (37)
\end{aligned}$$

where  $h$  is the overall rate of heat radiation delivered to a layer with average mass density  $\rho$ .

In what follows, we wish to develop constitutive equations for the flow of gas and liquid phases in deformable porous media consisting of two thin layers. The resulting equations can be readily extended to a system of multilayers of thin porous media. For later reference and better illustration, in Table 2, we list all relevant macroscale balance equations and continuity conditions for the problem under study.

### 7.2. Constitutive equations

As presented in Table 2, for a given system of two layers of thin porous media with solid, gas, and liquid as the three phases, we have a total of 24 governing equations (12 equations for each layer: three for mass, eight for momentum, and one for energy). It is worth noting that we exclude the through-plane motion equation for the solid phase in each layer. In principle, these governing equations should be solved to determine primary field variables (i.e. primary unknowns), which in our case are:

$$\{b, \varepsilon, s^l, \rho^{\alpha}, \mathbf{v}^{\alpha} (\alpha \neq s), \mathbf{F}_h^s, \theta\}_{k=1,2} \quad (38)$$

These variables are observable and measurable. But, governing equations also contain many variables which usually cannot be measured directly. Those variables in our case are:

**Table 2**

Balance equations and jump conditions for two interacting thin porous layers.

Description	Equations (phase indicator: $\alpha = s, g, l$ ; layer index: $k = 1, 2$ )
<i>Balance equations</i>	
Mass conservation (1 equation per phase per layer)	$\frac{D_h^x}{Dt} (b\epsilon^x \rho^x) \Big _k + b\epsilon^x \rho^x \nabla_h \cdot \mathbf{v}_h^x \Big _k = \epsilon^x \rho^x (e_x^T + e_x^B) \Big _k$
Momentum conservation (3 equations per phase per layer expect for solid phase)	$b\epsilon^x \rho^x \frac{D_h^x \mathbf{v}^x}{Dt} \Big _k - \nabla_h \cdot (b\mathbf{t}_h^x) \Big _k - b\epsilon^x \rho^x \mathbf{g}^x \Big _k - b\epsilon^x \rho^x \mathbf{T}^x \Big _k = \epsilon^x \rho^x (\mathbf{T}_x^T + \mathbf{T}_x^B) \Big _k$
Global energy conservation (1 equation per layer)	$\sum_x b\epsilon^x \rho^x \frac{D_h^x E^x}{Dt} \Big _k - \sum_x b\mathbf{t}_h^x \cdot \nabla_h \mathbf{v}^x \Big _k - \sum_x \nabla_h \cdot (b\mathbf{q}_h^x) \Big _k - \sum_x b\epsilon^x \rho^x h^x \Big _1 - \sum_x b\epsilon^x \rho^x Q^x \Big _k = \sum_x \epsilon^x \rho^x (Q_x^T + Q_x^B) \Big _k$
Entropy balance	$b\epsilon^x \rho^x \frac{D_h^x S^x}{Dt} \Big _k - \nabla_h \cdot (b\psi_h^x) \Big _k - b\epsilon^x \rho^x l^x \Big _k - b\epsilon^x \rho^x \Phi^x \Big _k = b\epsilon^x \rho^x \Gamma^x \Big _k + \epsilon^x \rho^x (\Phi_x^T + \Phi_x^B) \Big _k$
<i>Continuity conditions at the phase interfaces</i>	
Mass exchange	None
Momentum exchange	$\sum_x \epsilon^x \rho^x \mathbf{T}^x \Big _k = 0$
Energy exchange	$\sum_x \epsilon^x \rho^x (Q^x + \mathbf{T}^x \cdot \mathbf{v}^x) \Big _k = 0$
Entropy exchange	$\sum_x \epsilon^x \rho^x \Phi^x \Big _k = 0$
<i>Continuity conditions at the layer-layer boundary</i>	
Mass exchange	$\epsilon^x \rho^x e_x^B \Big _1 + \epsilon^x \rho^x e_x^T \Big _2 = 0$
Momentum exchange	$\epsilon^x \rho^x (\mathbf{v}^x e_x^B + \mathbf{T}_x^B) \Big _1 + \epsilon^x \rho^x (\mathbf{v}^x e_x^T + \mathbf{T}_x^T) \Big _2 = 0$
Energy exchange	$\epsilon^x \rho^x \left\{ \left[ E^x + \frac{1}{2} (\nu^x)^2 \right] e_x^B + Q_x^B + \mathbf{T}_x^B \cdot \mathbf{v}^x \right\} \Big _1 + \epsilon^x \rho^x \left\{ \left[ E^x + \frac{1}{2} (\nu^x)^2 \right] e_x^T + Q_x^T + \mathbf{T}_x^T \cdot \mathbf{v}^x \right\} \Big _2 = 0$
Entropy exchange	$\epsilon^x \rho^x (S^x e_x^B + \Phi_x^B) \Big _1 + \epsilon^x \rho^x (S^x e_x^T + \Phi_x^T) \Big _2 = 0$

$$\{\mathbf{t}_x^x, \mathbf{T}^x, A^x, S^x, \mathbf{q}_h^x, Q^x\}_{k=1,2}, \quad e_x^B \Big|_1, \quad \mathbf{T}_x^B \Big|_1, \quad Q_x^B \Big|_1 \quad (39)$$

Note that  $e_x^T \Big|_2$ ,  $\mathbf{T}_x^T \Big|_2$ , and  $Q_x^T \Big|_2$  are not listed here, because they are determined by the restrictions (Eqs. (25) and (27)–(29)).

The quantities listed in (39) are assumed to depend on primary variables (38) as well as their spatial derivatives. That is, we have the following set of independent variables:

$$\{b, \nabla_h b, \epsilon, \nabla_h \epsilon, s^l, \nabla_h s^l, \rho^x, \mathbf{v}^{x,s}, \mathbf{E}^s, \theta, \nabla_h \theta\}_{k=1,2} \quad (40)$$

The choice of independent variables is based on the expected behavior of the phases and our knowledge of internal state variables of the system. For example, the temperature gradient is included because it causes heat conduction inside the system. Absence of the velocity gradients is due to the fact that the phases are considered to behave as nonviscous materials at the macro-scale. It is noted that all constitutive variables should be independent of the frame of the reference (i.e. they should be objective). Because velocities  $\mathbf{v}^x$  are not objective, instead we make use of the relative velocities  $\mathbf{v}^{x,s}$  as our independent variables. The same argument is applicable to the choice of strain tensor  $\mathbf{E}^s$  instead of the solid-phase motion,  $\mathbf{F}_h^s$ . We note that the dependent variables listed in (39) are functions only of the independent variables, while the independent variables are functions of time and space.

Compared to the 24 governing equations for the two layers, the primary variables given in (38) comprise 30 unknowns. So, there is a deficit of 6 equations in order to have a determinate system. This closure problem always arises in the application of mixture theory and averaging-thermodynamic approach to the description of multiphase flow in porous media. Following Hassanizadeh and Gray [22], we select the following 6 extra dependent variables in order to close the system of equations:

$$\{\dot{b}, \dot{\epsilon}, \dot{s}^l\}_{k=1,2} \quad (41)$$

where the overdot indicates the material derivative with respect to a reference frame. For instance:

$$\dot{b} = \frac{D_h^r}{Dt} b \quad (42)$$

The variables listed in (41) are assumed to be functions of independent variables (40).

In general, each dependent variable would be postulated to depend on all independent variables. But, we make two exceptions. First, following the common practice in rational thermodynamics,

we use the constitutive assumptions that the entropy fluxes are solely due to heat input, and the entropy external source terms are only due to external energy sources. Thus, we would have:

$$\psi_h^x = \frac{\mathbf{q}_h^x}{\theta^x}, \quad l^x = \frac{h^x}{\theta^x} \quad (43)$$

There are also approaches where Eq. (43) are not assumed but are derived as equilibrium results (see e.g. [31]). Second, the dependence of free energies on velocities and gradients of saturation and temperature, as well as gradient of layer thickness, can be ruled out either because it may violate the second law of thermodynamics or based on intuitive understanding of the system under consideration [22]. Further, we postulate that the free energy of the  $\alpha$  phase in one layer is independent of the thermodynamic properties in the other layer. Thus, simpler functional dependencies for free energies are postulated as follows:

$$A^x \Big|_k = A^x(b, \rho^x, s^x, \theta) \Big|_k \quad \alpha = g, l \quad (44)$$

$$A^s \Big|_k = A^s(b, \rho^s, s^l, \theta, \mathbf{E}^s) \Big|_k \quad (45)$$

According to the axiom of admissibility, constitutive equations must not violate balance laws and the second law of thermodynamics given as the inequality (34). This axiom places some very important restrictions on the constitutive equations. Restrictions imposed by this requirement are explored by the method of Coleman and Noll [15]. The expansion of the second law of thermodynamics is presented in detail in Appendix C. Taking into account the thermodynamic definition of phase pressure (Eq. (C9)), the residual entropy inequality becomes:

$$\begin{aligned} \Lambda = & \sum_{k=1}^2 \sum_{\alpha} b\epsilon^x \rho^x \Gamma^x \Big|_k = \sum_{k=1}^2 \frac{D_h^s \mathcal{E}}{Dt} \left( \sum_{\alpha \neq s} \frac{b}{\theta} s^x p^x - \frac{b}{\theta} p^s \right) \Big|_k \\ & + \sum_{k=1}^2 \frac{D_h^s s^l}{Dt} \left[ \frac{b\epsilon^g \rho^g}{\theta} \frac{\partial A^g}{\partial s^g} - \frac{b\epsilon^l \rho^l}{\theta} \frac{\partial A^l}{\partial s^l} - \frac{b(1-\epsilon) \rho^s}{\theta} \frac{\partial A^s}{\partial s^l} + \frac{b\epsilon}{\theta} p^l \right. \\ & \left. - \frac{b\epsilon^g p^g}{\theta} \right] \Big|_k + \sum_{k=1}^2 \frac{D_h^s b}{Dt} \left[ \frac{(1-\epsilon) p^s}{\theta} - \frac{b(1-\epsilon) \rho^s}{\theta} \frac{\partial A^s}{\partial b} \right. \\ & \left. + \sum_{\alpha \neq s} \left( \frac{\epsilon s^x p^x}{\theta} - \frac{b\epsilon^x \rho^x}{\theta} \frac{\partial A^x}{\partial b} \right) \right] \Big|_k \\ & + \sum_{\alpha \neq s} \mathbf{v}_h^{x,s} \cdot \left[ \left( \frac{\epsilon s^x p^x}{\theta_1} - \frac{b\epsilon^x \rho^x}{\theta_1} \frac{\partial A^x}{\partial b} \right) \nabla_h b + \frac{b p^x}{\theta_1} \nabla_h (\epsilon s^x) \right] \end{aligned}$$

$$\begin{aligned}
& \left. -\frac{bes^\alpha \rho^\alpha}{\theta_1} \frac{\partial A^\alpha}{\partial s^\alpha} \nabla_h s^\alpha - \frac{be^\alpha \rho^\alpha}{\theta^\alpha} \mathbf{T}_h^\alpha - \frac{\varepsilon^\alpha \rho^\alpha \mathbf{T}_{hz}^\alpha}{\theta^\alpha} \right|_1 \\
& + \sum_{\alpha \neq s} \mathbf{v}_{\alpha,s}^\alpha \cdot \left[ \left( \frac{\varepsilon^\alpha p^\alpha}{\theta_2} - \frac{bes^\alpha \rho^\alpha}{\theta_2} \frac{\partial A^\alpha}{\partial b} \right) \nabla_h b + \frac{bp^\alpha}{\theta_2} \nabla_h (es^\alpha) \right. \\
& \left. - \frac{bes^\alpha \rho^\alpha}{\theta_2} \frac{\partial A^\alpha}{\partial s^\alpha} \nabla_h s^\alpha - \frac{be^\alpha \rho^\alpha}{\theta^\alpha} \mathbf{T}_h^\alpha - \frac{\varepsilon^\alpha \rho^\alpha \mathbf{T}_{hz}^\alpha}{\theta^\alpha} \right]_2 \\
& - \sum_{\alpha \neq s} \nu_{\alpha,v}^\alpha \left( \frac{be^\alpha \rho^\alpha}{\theta^\alpha} \mathbf{T}_v^\alpha + \frac{\varepsilon^\alpha \rho^\alpha T_{v\alpha}^\alpha}{\theta^\alpha} \right) \Big|_1 - \sum_{\alpha \neq s} \nu_{\alpha,v}^\alpha \left[ \frac{be^\alpha \rho^\alpha}{\theta^\alpha} \mathbf{T}_v^\alpha + \frac{\varepsilon^\alpha \rho^\alpha T_{v\alpha}^\alpha}{\theta^\alpha} \right]_2 \\
& + \sum_{\alpha} \varepsilon_1^\alpha \rho_1^2 e_\alpha^B \Big|_1 \left\{ \frac{p_2^\alpha}{\theta_2 \rho_2^\alpha} - \frac{p_1^\alpha}{\theta_1 \rho_1^\alpha} + \left( \frac{A_2^\alpha}{\theta_2} - \frac{A_1^\alpha}{\theta_1} \right) \right. \\
& \left. + \frac{1}{\theta^\alpha} \left[ \frac{1}{2} (\nu_{2,s}^\alpha)^2 - \frac{1}{2} (\nu_{1,s}^\alpha)^2 \right] + \frac{\theta^{2,r}}{\theta_2 \theta^\alpha} E_2^\alpha - \frac{\theta^{1,r}}{\theta_1 \theta^\alpha} E_1^\alpha \right\} \\
& + \sum_{k=1}^2 \left[ \sum_{\alpha} \frac{b \mathbf{q}_h^\alpha}{(\theta^\alpha)^2} - \sum_{\alpha \neq s} \frac{bes^\alpha \rho^\alpha}{\theta^\alpha} \left( \frac{\partial A^\alpha}{\partial \theta} + S^\alpha \right) \mathbf{v}_{\alpha,s}^\alpha \right] \cdot \nabla_h \theta|_k \\
& - \frac{\theta^{1,r}}{\theta_1 \theta^\alpha} \left( \sum_{\alpha} be^\alpha \rho^\alpha Q^\alpha \Big|_1 + \sum_{\alpha} \varepsilon^\alpha \rho^\alpha Q_\alpha^B \Big|_1 \right) \\
& - \frac{\theta^{2,r}}{\theta_2 \theta^\alpha} \left( \sum_{\alpha} be^\alpha \rho^\alpha Q^\alpha \Big|_2 + \sum_{\alpha} \varepsilon^\alpha \rho^\alpha Q_\alpha^T \Big|_2 \right) \geq 0 \quad (46)
\end{aligned}$$

### 7.3. Equilibrium restrictions

The inequality (46) expresses the fact that the rise in the entropy of the system is due to the changes in porosity, saturation, and layer thickness, fluid flow (relative to the solid) in each layer, heat transport, and mass exchange between layers. All of these processes are known to vanish under equilibrium condition. We can extract additional restrictions on constitutive functions by examining the residual inequality at equilibrium. First, the state of thermodynamic equilibrium is defined to be the state at which the following variables all vanish:

$$\{z_\mu\} = \left\{ \left( \mathbf{v}^{\alpha,s}, \nabla_h \theta, \dot{e}, \dot{S}, \dot{b} \right) \Big|_{k=1,2}, \theta^{1,r}, \theta^{2,r}, e_\alpha^B \Big|_1 \right\} \quad (47)$$

This means that at equilibrium, inside either layer, there are no relative movements of phases, the heat conduction vanishes, and the rates of changes of the porosity, saturation and layer thickness are all zero. In addition, there are no temperature difference and mass exchange between the two layers. One can readily verify that the total entropy production rate  $\Lambda$ , given by (46), would be zero at equilibrium. Given the fact that  $\Lambda$  is always non-negative, this means that it reaches its minimum value at equilibrium. The necessary and sufficient conditions for  $\Lambda$  to be a minimum at equilibrium are:

$$\left( \frac{\partial \Lambda}{\partial z_\mu} \right)_e = 0 \quad (48)$$

$$\left\| \left( \frac{\partial^2 \Lambda}{\partial z_\mu \partial z_\lambda} \right)_e \right\| \text{ be positive semi-definite} \quad (49)$$

Here, the subscript  $e$  behind the parenthesis indicates that the function is evaluated at equilibrium. These two conditions place restrictions on constitutive functions. In particular, imposition of Eq. (48) yields a number of equilibrium relationships, which are given shortly. Requirement (49) imposes restrictions on the sign of material coefficients, as shown at the end of Section 7.

As an example of how Eq. (48) leads to equilibrium restrictions, consider the first term in inequality (46). Because  $\dot{e}$  is one of the variables that vanish at equilibrium (see list (47)), imposition of (48) results in:

$$\left( \sum_{\alpha \neq s} \frac{b}{\theta} s^\alpha p^\alpha - \frac{b}{\theta} p^s \right)_e = 0 \quad (50a)$$

Rearranging this equation, we find that, at equilibrium, the solid phase pressure is equal to the weighted sum of fluid phase pressures:

$$(p^s)_e = \left[ (s^l p^l + s^g p^g) \Big|_k \right]_e \quad (50b)$$

The difference in fluid pressures is related to the rate of change of free energies of all phases due to a change in saturation:

$$(p^g - p^l)_e = s^g \rho^g \frac{\partial A^g}{\partial s^g} - s^l \rho^l \frac{\partial A^l}{\partial s^l} - \frac{(1-\varepsilon) \rho^s}{\varepsilon} \frac{\partial A^s}{\partial s^l} \quad (51)$$

where the r.h.s provides a thermodynamic definition of macroscopic capillary pressure,  $p^c$ :

$$p^c = s^g \rho^g \frac{\partial A^g}{\partial s^g} - s^l \rho^l \frac{\partial A^l}{\partial s^l} - \frac{(1-\varepsilon) \rho^s}{\varepsilon} \frac{\partial A^s}{\partial s^l} \quad (52)$$

Note that when the layer index  $k$  is omitted, it means that the equation holds in the same form for each layer. It is worth noting that our definition of macroscopic capillary pressure is different from that of Hassanizadeh and Gray [22]. This is because in the present work, we assumed that phase interfaces do not possess any thermodynamic properties.

The solid phase pressure in each layer is related to the change of free energies of all phases in the layer as a result of change in the layer thickness:

$$(p^s)_e = b(1-\varepsilon) \rho^s \frac{\partial A^s}{\partial b} + bes^l \rho^l \frac{\partial A^l}{\partial b} + bes^g \rho^g \frac{\partial A^g}{\partial b} \quad (53)$$

The fourth and fifth summation terms in inequality (46) provide the equilibrium parts of the momentum exchange terms. For the first layer, the equilibrium part of momentum exchange for the  $\alpha$  phase is given as:

$$\begin{aligned}
& \left( be^\alpha \rho^\alpha \mathbf{T}_h^\alpha + \varepsilon^\alpha \rho^\alpha \mathbf{T}_{hz}^\alpha \right)_e = \left[ \left( \varepsilon^\alpha p^\alpha - bes^\alpha \rho^\alpha \frac{\partial A^\alpha}{\partial b} \right) \nabla_h b + bp^\alpha \nabla_h (es^\alpha) \right. \\
& \left. - bes^\alpha \rho^\alpha \frac{\partial A^\alpha}{\partial s^\alpha} \nabla_h s^\alpha \right]_1 \quad \alpha = g, l \quad (54)
\end{aligned}$$

Obviously, the momentum exchange term also has a nonequilibrium part, which we denote by  $\tau_h^\alpha$  (L/T<sup>2</sup>). Thus, the following general equation can be given for the momentum exchange term:

$$\begin{aligned}
& \left( be^\alpha \rho^\alpha \mathbf{T}_h^\alpha + \varepsilon^\alpha \rho^\alpha \mathbf{T}_{hz}^\alpha \right)_e = \left[ \underbrace{\left( \varepsilon^\alpha p^\alpha - bes^\alpha \rho^\alpha \frac{\partial A^\alpha}{\partial b} \right) \nabla_h b + bp^\alpha \nabla_h (es^\alpha) - bes^\alpha \rho^\alpha \frac{\partial A^\alpha}{\partial s^\alpha} \nabla_h s^\alpha}_{\text{equilibrium}} + \underbrace{bes^\alpha \rho^\alpha \tau_h^\alpha}_{\text{nonequilibrium}} \right]_1 \quad \alpha = g, l \quad (55)
\end{aligned}$$

The nonequilibrium part of momentum exchange term is a function of the full set of independent variables listed in (43). Similar formulae are found for layer 2.

The eighth summation term in inequality (46) results in the following equality at equilibrium (note that relative velocities and temperature differences vanish at equilibrium):

$$\left( A^\alpha + \frac{p^\alpha}{\rho^\alpha} \right)_e = \left( A^\alpha + \frac{p^\alpha}{\rho^\alpha} \right)_2 \quad (56)$$

The combination of terms in Eq. (56) is equal to the Gibbs free energy. Thus, Eq. (56) prescribes the following equilibrium restriction:

$$(G_1^\alpha)_e = (G_2^\alpha)_e \quad (57)$$

The ninth summation term in equality (46) leads to the result that there is no heat flux within the layers at equilibrium:

$$(\mathbf{q}_h^\alpha|_k)_e = 0 \quad (58)$$

Finally, the last two terms in equality (46) show that the sum of the heat exchanges of the  $\alpha$  phase with all other phases inside the layer and with the  $\alpha$  phase in the neighboring layer is equal to zero:

$$[(b\epsilon^\alpha \rho^\alpha Q^\alpha + \epsilon^\alpha \rho^\alpha Q_\alpha^B)]_1 = 0 \quad (59a)$$

$$[(b\epsilon^\alpha \rho^\alpha Q^\alpha + \epsilon^\alpha \rho^\alpha Q_\alpha^T)]_2 = 0 \quad (59b)$$

#### 7.4. Linearization

To this point, the developed equations are quite general. For some problems, additional simplifications can be obtained by considering the dynamics of the system 'near' equilibrium, where the listed variables in (47) are small enough to allow a linear dependence of constitutive functions.

In this subsection, we focus our attention on the flow of the two fluids inside each layer as well as the mass and heat exchanges between the two layers. First, consider the momentum conservation equation (15) for the first layer. Neglect inertia terms (which is a common assumption in porous media theories) and use Eqs. (C8) and (55) to obtain:

$$\begin{aligned} \nabla_h(p^\alpha)|_1 - \rho^\alpha \mathbf{g}_h|_1 &= -\rho^\alpha \frac{\partial A^\alpha}{\partial b} \nabla_h b \Big|_1 - \frac{\Omega^\alpha}{s^\alpha} \nabla_h s^\alpha \Big|_1 + \rho^\alpha \mathbf{t}_h^\alpha \Big|_1 + \frac{\rho^\alpha}{b} \mathbf{T}_{ha}^T \Big|_1 \\ &\quad - \frac{\theta^{1,r}}{\theta_1} \left[ \left( \frac{p^\alpha}{b} - \rho^\alpha \frac{\partial A^\alpha}{\partial b} \right) \nabla_h b + \frac{p^\alpha \nabla_h(\epsilon s^\alpha)}{\epsilon s^\alpha} \right. \\ &\quad \left. - \frac{\Omega^\alpha}{s^\alpha} \nabla_h s^\alpha + \rho^\alpha \mathbf{t}_h^\alpha \right] \Big|_1 \quad \alpha = g, l \end{aligned} \quad (60)$$

where  $\Omega^\alpha$  is called the wettability potential [22], defined by:

$$\Omega^\alpha = s^\alpha \rho^\alpha \frac{\partial A^\alpha}{\partial s^\alpha} \quad (61)$$

A similar equation is obtained for the second layer. In Eq. (60), the l.h.s is the common driving force in porous media flow. On the r.h.s., the first two terms account for the effects of the gradients of layer thickness and saturation on the fluid flow; the third term is the nonequilibrium part of the momentum exchange term; the fourth term is provided by boundary condition at the top of layer 1; and the last grouped term accounts for the possibility of flow due to a temperature difference between two neighboring layers.

As mentioned earlier, the dissipative drag force  $\mathbf{t}_h^\alpha$  is still a function of all independent variables listed in (40). But, if the deviation of the system from equilibrium is small, this force may be assumed to be a linear function of the independent variable  $\mathbf{v}_h^{\alpha,s}$ :

$$\mathbf{t}_h^\alpha = -\mathbf{R}_g^\alpha \cdot \mathbf{v}_h^{\alpha,s} - \mathbf{R}_l^\alpha \cdot \mathbf{v}_h^{l,s} \quad \alpha = g, l \quad (62)$$

where the 2D tensors  $\mathbf{R}_g^\alpha$  and  $\mathbf{R}_l^\alpha$  are material coefficients that may depend on  $b, \epsilon, s^l, \rho^\alpha$ , and  $\theta$ . Note that  $\mathbf{t}_h^\alpha$  is not allowed to be linearly dependent on the variables  $\nabla_h b, \nabla_h \epsilon, \nabla_h s^l$  and  $\mathbf{E}^s$ . This is because these variables are not necessarily zero at equilibrium, whereas  $\mathbf{t}_h^\alpha$  must vanish at equilibrium.

Second, the entropy inequality (46) indicates that the  $\alpha$ -phase mass exchange between the two layers arises from the differences in the temperature-weighted Gibbs free energies, kinetic energies and internal energies. For the linear case under consideration here, the following relationship is postulated:

$$\epsilon_1^\alpha \rho_1^\alpha e_\alpha^B \Big|_1 = \Pi_m \left\{ \left( \frac{G_2^\alpha}{\theta_2} - \frac{G_1^\alpha}{\theta_1} \right) + \frac{1}{\theta^r} \left[ \frac{1}{2} (\nu_2^{\alpha,s})^2 - \frac{1}{2} (\nu_1^{\alpha,s})^2 \right] + \frac{\theta^{2,r}}{\theta_2 \theta^r} F_2^\alpha - \frac{\theta^{1,r}}{\theta_1 \theta^r} F_1^\alpha \right\} \quad (63)$$

where  $\Pi_m$  is a general material coefficient which must be determined experimentally.

Away from equilibrium, the layer thickness  $b$  may change with time, e.g. due to swelling and shrinkage (solid phase motion). The third summation term in inequality (46) suggests that  $b$  may be a linear function of the term multiplying it:

$$b = \Pi_b \left[ (1 - \epsilon) p^s - b(1 - \epsilon) p^s \frac{\partial A^s}{\partial b} + \sum_{\alpha \neq s} \left( \epsilon s^\alpha p^\alpha - b \epsilon s^\alpha \rho^\alpha \frac{\partial A^\alpha}{\partial b} \right) \right] \quad (64)$$

where  $\Pi_b$  is also a material coefficient which also must be determined experimentally.

Next, consider the time rate of change of liquid saturation,  $s^l$ , appearing in the second summation term of the entropy inequality (46). A linear dependence of  $s^l$  on the term multiplying it may be assumed. Given the definition of capillary pressure (Eq. (52)), we obtain:

$$\dot{s}^l = -\Pi_{s^l} (p^g - p^l - p^c) \quad (65)$$

where  $\Pi_{s^l}$  is a material coefficient. This equation indicates that the pressure difference in fluids is equal to capillary pressure but only at equilibrium. The nonequilibrium capillary effect has been the subject of many studies [26,27] and it is shown to be significant under certain conditions.

Examination of the ninth summation term of the inequality (46) suggests the following linear equation for the overall heat flux vector in each layer:

$$\sum_\alpha b \mathbf{q}_h^\alpha - \sum_{\alpha \neq s} b \epsilon s^\alpha \rho^\alpha \theta \left( \frac{\partial A^\alpha}{\partial \theta} + S^\alpha \right) \mathbf{v}^{\alpha,s} = \mathbf{K} \cdot \nabla_h \theta \quad (66)$$

where  $\mathbf{K}$  is a material property. Finally, the overall heat exchange terms for each layer can be described by the following linearized equations:

$$\sum_\alpha \left( b \epsilon^\alpha \rho^\alpha Q^\alpha + \epsilon^\alpha \rho^\alpha Q_\alpha^B \right) \Big|_1 = -\bar{K}_1 (\theta_1 - \theta^r) \quad (67a)$$

$$\sum_\alpha \left( b \epsilon^\alpha \rho^\alpha Q^\alpha + \epsilon^\alpha \rho^\alpha Q_\alpha^T \right) \Big|_2 = -\bar{K}_2 (\theta_2 - \theta^r) \quad (67b)$$

where  $\bar{K}_1$  and  $\bar{K}_2$  are material properties which may be functions of  $\rho^\alpha, \epsilon, b, s^l$ , and  $\theta$  in both layers.

If we substitute the linearized constitutive relationships postulated above back into Eq. (46), and neglect the contribution of  $\dot{\epsilon}$  to the rate of entropy production, the entropy inequality becomes:

$$\begin{aligned} \Lambda &= \sum_{k=1}^2 \sum_\alpha b \epsilon^\alpha \rho^\alpha \Gamma^\alpha \Big|_k = \sum_{k=1}^2 b \epsilon (s^l)^2 (\Pi_{s^l})^{-1} \Big|_k + \sum_{k=1}^2 \frac{1}{\theta} (\dot{b})^2 (\Pi_b)^{-1} \Big|_k \\ &\quad + \sum_{k=1}^2 \sum_{\alpha \neq s} \sum_{\beta \neq s} \frac{b \epsilon s^\alpha \rho^\alpha}{\theta} \mathbf{v}^{\alpha,s} \cdot \mathbf{R}_\beta^\alpha \cdot \mathbf{v}^{\beta,s} \Big|_k + \sum_\alpha \left( \epsilon_1^\alpha \rho_1^\alpha e_\alpha^B \Big|_1 \right)^2 (\Pi_m)^{-1} \\ &\quad + \sum_{k=1}^2 \sum_\alpha \frac{1}{(\theta)^2} \nabla_h \theta \cdot \mathbf{K} \cdot \nabla_h \theta \Big|_k + \frac{(\theta^{1,r})^2}{\theta_1 \theta^r} \bar{K}_1 + \frac{(\theta^{2,r})^2}{\theta_2 \theta^r} \bar{K}_2 \geq 0 \end{aligned} \quad (68)$$

Imposition of the second condition of equilibrium (Eq. (49)) results in the following restrictions on these material coefficients:

$$\{\Pi_{s^l}, \Pi_b, \Pi_m, \bar{K}\}_{k=1,2} \geq 0 \quad (69a)$$

$$\left\{ \mathbf{R}_\beta^\alpha + \left( \mathbf{R}_\alpha^\beta \right)^T, \mathbf{K} \right\}_{k=1,2} \text{ are positive semi-definite tensors} \quad (69b)$$

#### 8. Simplified governing equations for air–water flow and heat transfer within two thin porous layers

In this section, we develop simplified governing equations for flow and heat transfer in a system of two thin porous layers con-

taining air and water. The relevant equations are the mass balance (10), the linearized momentum balance (60), and the overall energy balance (37) augmented with the linearized constitutive equations developed in the previous section. Moreover, we make the following assumptions that are valid for most typical porous media applications. The solid phase is assumed to be rigid and stationary with prespecified distributions of layer thickness and porosity. We assume incompressible fluids and slow flow. In addition, it is assumed that the driving force for mass exchange between the two layers is dominated by the difference in fluid pressures; that is, the remaining terms on the r.h.s. of Eq. (63) may be neglected (note that the justification of this assumption is provided in detail in [Appendix D](#)).

First, with these assumptions, the mass conservation equations for two fluid phases are reduced to the following forms:

$$\frac{\partial s^x}{\partial t} \Big|_1 + \nabla_h \cdot (s^x \mathbf{v}_h^x) \Big|_1 = \frac{1}{b\varepsilon(\rho^x)^2} \Big|_1 \Pi_m \left( \frac{p_2^x}{\theta_2} - \frac{p_1^x}{\theta_1} \right) + \frac{s^x}{b} e_x^T \Big|_1 \quad (70)$$

$$\frac{\partial s^x}{\partial t} \Big|_2 + \nabla_h \cdot (s^x \mathbf{v}_h^x) \Big|_2 = -\frac{1}{b\varepsilon(\rho^x)^2} \Big|_2 \Pi_m \left( \frac{p_2^x}{\theta_2} - \frac{p_1^x}{\theta_1} \right) + \frac{s^x}{b} e_x^B \Big|_2 \quad (71)$$

The last terms on the r.h.s. of the equations are considered to be known and provided by the top and bottom boundary conditions, respectively.

Then, consider the momentum balance Eq. (60). We take the average temperature of the two layers as the reference temperature ( $\theta^r = (\theta_1 + \theta_2)/2$ ). Furthermore, we make the following assumptions: (1) neglect the fluid motion due to thermal effects; (2) neglect the coupling effect of motion of the two fluids; and (3) layer-thickness variations are negligible. As a result, the following Darcy-type equations are obtained:

$$\mathbf{v}_h^x \Big|_1 = \left\{ -\frac{\mathbf{K}^x}{\varepsilon s^x} \left[ \nabla_h(p^x) - \rho^x \mathbf{g}_h + \frac{\Omega^x}{s^x} \nabla_h s^x - \frac{\rho^x}{b} \mathbf{T}_{hx}^T \right] \right\} \Big|_1 \quad (72)$$

$$\mathbf{v}_h^x \Big|_2 = \left\{ -\frac{\mathbf{K}^x}{\varepsilon s^x} \left[ \nabla_h(p^x) - \rho^x \mathbf{g}_h + \frac{\Omega^x}{s^x} \nabla_h s^x - \frac{\rho^x}{b} \mathbf{T}_{hx}^B \right] \right\} \Big|_2 \quad (73)$$

where the terms  $\mathbf{T}_{hx}^T$  and  $\mathbf{T}_{hx}^B$  are considered to be provided by boundary conditions, and  $\mathbf{K}^x = \varepsilon s^x / \rho^x \mathbf{R}^x$  denotes the  $\alpha$ -phase conductivity tensor which is a material coefficient.

Next, neglecting the heat dissipation term, and substitution of Eqs. (66) and (67) into the overall energy equation (38) for each layer, we can obtain:

$$\sum_x b\varepsilon s^x \rho^x C^x \frac{\partial \theta}{\partial t} \Big|_1 + \sum_{x \neq s} b\varepsilon s^x \rho^x C^x \mathbf{v}_h^x \cdot \nabla_h \theta \Big|_1 - \nabla_h \cdot (\mathbf{K} \cdot \nabla_h \theta) \Big|_1 - \sum_x b\varepsilon s^x \rho^x h^x \Big|_1 = \bar{K}(\theta_2 - \theta_1) + \sum_x \varepsilon s^x \rho^x Q_x^T \Big|_1 \quad (74)$$

$$\sum_x b\varepsilon s^x \rho^x C^x \frac{\partial \theta}{\partial t} \Big|_2 + \sum_{x \neq s} b\varepsilon s^x \rho^x C^x \mathbf{v}_h^x \cdot \nabla_h \theta \Big|_2 - \nabla_h \cdot (\mathbf{K} \cdot \nabla_h \theta) \Big|_2 - \sum_x b\varepsilon s^x \rho^x h^x \Big|_2 = -\bar{K}(\theta_2 - \theta_1) + \sum_x \varepsilon s^x \rho^x Q_x^B \Big|_2 \quad (75)$$

where  $C^x = \partial E^x / \partial \theta$  is called the mass-specific heat capacity ( $\text{L}^2/\text{T}^2$ ) of the  $\alpha$  phase (i.e. solid, air, or water phase),  $\mathbf{K}$  is the heat conductivity of the layer, and  $\bar{K}$  is the heat exchange coefficient between the two layers. The term  $\bar{K}(\theta_2 - \theta_1)$  accounts for the heat exchange between the two layers. In addition, to reach the above form of overall energy equations, we assumed that the second term on the l.h.s. of Eq. (66) could be neglected. This term arises from the assumption of local thermal equilibrium (see Eq. (36)). If releasing this assumption, one would obtain the constitutive relationship of

$\partial A^x / \partial \theta^x + S^x = 0$  (refer to [\[22\]](#)). The last term on the r.h.s. of each heat transport equation is provided by boundary condition.

Finally, in each layer, the air and water pressures are related by the following constitutive equation:

$$p^g - p^l = p^c - (\Pi_{s^l})^{-1} s^l \quad (76)$$

To sum up, assuming that all material coefficients (i.e.  $\Pi_m$ ,  $\mathbf{K}^x|_k$ ,  $\mathbf{K}|_k$ ,  $\bar{K}$ , and  $\Pi_{s^l}$ ) are known for the two-layer system considered in this case study, we have a total of 18 governing and closure equations (i.e. Eqs. (70)–(76) and (3a)). They can be solved together with proper boundary conditions to determine 18 primary field variables  $\{s^x, \mathbf{v}_h^x, p^x, \theta\}|_k$  ( $\alpha = g, l; k = 1, 2$ ).

## 9. Discussion and conclusions

To overcome a number of shortcomings in the traditional Darcy-based 3D descriptions of multiphase flow and solute transport through multilayers of thin porous media, we have reformulated macroscale governing equations by employing the averaging-thermodynamic approach. Based on an REV defined for each layer, we averaged microscale transport equations over the layer thickness. As a result, we obtained a set of 2D governing equations along with a number of exchange terms accounting for the exchanges of mass, momentum, and energy between two neighboring layers.

Next, we exploited the second law of thermodynamics in order to develop constitutive equations that account for material behaviors. Without losing generality, we considered a system of two thin porous layers with solid, gas, and liquid as the three phases. In addition, for simplification we switched off some intra-layer processes (i.e. phase change and heat exchange among phases). For cases that the dynamics of the system is 'near' equilibrium, we derived the equation of fluid motion inside each layer. This equation reduces to the classical Darcy's law, if neglecting the coupling effect between the motions of phases, neglecting the fluid motion due to thermal effects, and neglecting the effect of variations in layer thickness and saturation.

According to linearization theory, the constitutive equations for exchange terms appearing in governing equations have been derived, which are listed in [Table 3](#). First, the difference in temperature-density-weighted phase pressures was found to be the main driving force for the mass exchange of any phase between two neighboring layers. The verification of this conclusion was detailed in [Appendix D](#). Second, the overall  $\alpha$ -phase momentum exchange term includes both equilibrium and nonequilibrium parts. The nonequilibrium part was assumed to be a linear function of the phase velocity. As a result, the fluid motion equation was obtained as shown in Eq. (60). Last, the overall  $\alpha$ -phase energy exchange was found to be linearly proportional to the temperature difference between two neighboring layers. Note that the signs of the appeared material coefficients in these terms were given in Eq. (69a). They may be functions of  $\rho^x$ ,  $\varepsilon$ ,  $b$ ,  $s^l$ , and  $\theta$  in both layers. But, their precise functional forms need to be determined experimentally.

As a demonstration of the applicability of the model, based on several assumptions which are valid for most typical porous media applications, we have presented the simplified governing equations for a system of air–water flow and heat transfer within two thin porous layers. These equations can be solved to obtain fluid saturations and temperature fields within the layers. It is worth noting that the present results derived for a system of two layers of thin porous media are ready to be extended into a system of  $N$  thin porous layers, if we assume that the exchanges of mass, momentum, and energy at a layer–layer boundary, are solely

**Table 3**

Exchange terms for mass, momentum, and energy between the two thin porous layers.

Exchanged quantity	Constitutive equation	Description
Mass	$\varepsilon_1^x \rho_1^x e_x^B  _1 = -\varepsilon_2^x \rho_2^x e_x^T  _2 = \Pi_m \left( \frac{p_1^x}{\theta_2 \rho_2^x} - \frac{p_2^x}{\theta_1 \rho_1^x} \right)$	The simplified mass exchange term as shown in <a href="#">Appendix D</a>
Momentum	$\left( b \varepsilon^x \rho^x \mathbf{T}_h^x + \varepsilon^x \rho^x \mathbf{T}_{hx}^B \right)  _1 = \frac{\theta'}{\theta_1} \left[ \underbrace{\left( \varepsilon^x p^x - b \varepsilon^x \rho^x \frac{\partial A^x}{\partial b} \right) \nabla_h b + b p^x \nabla_h (\varepsilon^x) - b \varepsilon^x \rho^x \frac{\partial A^x}{\partial S^x} \nabla_h S^x}_{\text{equilibrium}} + \underbrace{b \varepsilon^x \rho^x \mathbf{T}_h^x}_{\text{non-equilibrium}} \right]  _1$	The momentum exchange term for the first layer including equilibrium part and nonequilibrium part (see Eq. <a href="#">(62)</a> )
	$\left( b \varepsilon^x \rho^x \mathbf{T}_h^x + \varepsilon^x \rho^x \mathbf{T}_{hx}^T \right)  _2 = \frac{\theta'}{\theta_1} \left[ \underbrace{\left( \varepsilon^x p^x - b \varepsilon^x \rho^x \frac{\partial A^x}{\partial b} \right) \nabla_h b + b p^x \nabla_h (\varepsilon^x) - b \varepsilon^x \rho^x \frac{\partial A^x}{\partial S^x} \nabla_h S^x}_{\text{equilibrium}} + \underbrace{b \varepsilon^x \rho^x \mathbf{T}_h^T}_{\text{non-equilibrium}} \right]  _2$	The momentum exchange term for the second layer
Energy	$\sum_x \left( b \varepsilon^x \rho^x Q^x + \varepsilon^x \rho^x Q_x^B \right)  _1 = \bar{K}(\theta_2 - \theta_1)$ $\sum_x \left( b \varepsilon^x \rho^x Q^x + \varepsilon^x \rho^x Q_x^T \right)  _2 = -\bar{K}(\theta_2 - \theta_1)$	The energy exchange term for the first layer The energy exchange term for the second layer

determined by the differences in thermodynamic quantities pertinent to two adjacent layers.

Finally, we give some perspectives on coping with imperfect contact between layers (mainly due to inherent roughness of surfaces), which may exist in some engineering applications of thin porous media [\[28\]](#). Although the present model was derived based on the assumption of no gap between layers, it is possible and reasonable to include the effect of imperfect contact into the material coefficient  $\Pi_m$  which appears in the mass exchange term between two neighboring layers (see Eqs. [\(70\)](#) and [\(71\)](#)). In other words, the material coefficient  $\Pi_m$  is a material property of two neighboring layers as well as their boundary morphology.

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## Appendix A. Averaging of microscopic balance equation and the associated definition of macroscopic thermodynamic quantities

At the microscopic scale, the governing equations for each phase are the classical balance laws of continuum mechanics, which may be stated in the following general form

$$\frac{\partial(\rho\psi)}{\partial t} + \nabla \cdot (\rho\mathbf{v}\psi) - \nabla \cdot \mathbf{i} - \rho\lambda = \rho G \quad (\text{A1})$$

where  $\rho$  is the mass density,  $\psi$  is a typical thermodynamic property (mass, momentum, energy, or entropy),  $\mathbf{v}$  is the velocity vector,  $\mathbf{i}$  is the contact flux vector,  $\lambda$  is the external supply, and  $G$  denotes the rate of net production. Prior to averaging Eq. [\(A1\)](#) over the REV for a layer (see [Fig. 2](#)), we define the following macroscopic (REV-scale) quantities and present the necessary spatial and temporal averaging theorems.

### A.1. Macroscopic definitions

$$\text{Volume fraction of the } \alpha \text{ phase : } \varepsilon^\alpha = \frac{1}{b\delta A} \int_{\delta V} \gamma_\alpha d\nu \quad (\text{A2})$$

where  $b$  is the average thickness of the REV,  $\delta A$  is the cross-sectional area of the REV,  $\delta V$  is the volume of the REV, and  $\gamma_\alpha$  is the phase distribution function which has the value of unity inside the phase and zero outside the phase.

$$\text{Volume-averaged quantity : } \langle f \rangle_\alpha = \frac{1}{b\delta A} \int_{\delta V} f \gamma_\alpha d\nu \quad (\text{A3})$$

$$\begin{aligned} \text{Intrinsic volume-averaged quantity } \langle f \rangle_\alpha^x &= \frac{1}{b\varepsilon^\alpha \delta A} \int_{\delta V} f \gamma_\alpha d\nu \\ &= \frac{1}{b\varepsilon^\alpha \delta A} \int_{\delta V} f \gamma_\alpha d\nu \end{aligned} \quad (\text{A4})$$

$$\text{Mass-averaged quantity } f^\alpha = \frac{1}{\langle \rho \rangle_\alpha b \delta A} \int_{\delta V} \rho f \gamma_\alpha d\nu \quad (\text{A5})$$

In Eqs. [\(A3\)](#)–[\(A5\)](#),  $f$  is a general thermodynamic quantity, and it is seen that  $\langle f \rangle_\alpha = \varepsilon^\alpha \langle f \rangle_\alpha^x$ . We note that for averaging thermodynamic quantities, the integrand multiplied by an infinitesimal element of integration must be an additive quantity [\[13\]](#). Therefore, the mass-averaged operation (see Eq. [\(A5\)](#)) is normally preferred when defining macroscopic thermodynamic quantities.

### A.2. Spatial averaging theorem

This theorem relates the average of a gradient to the gradient of an average. When taking the average of the 3D gradient of a function over the  $\alpha$  phase, we can get:

$$\begin{aligned} \langle \nabla f \rangle_\alpha &= \frac{1}{b\delta A} \int_{\delta V} \gamma_\alpha \nabla f d\nu \\ &= \frac{1}{b\delta A} \int_{\delta V} \nabla(\gamma_\alpha f) d\nu - \frac{1}{b\delta A} \int_{\delta V} f \nabla \gamma_\alpha d\nu \end{aligned} \quad (\text{A6})$$

Since  $\delta A$  and  $\delta V$  are independent of position, we can move the gradient operator out of the integral for the first term on the r.h.s. of Eq. [\(A6\)](#). Then, we get the form:

$$\begin{aligned} \langle \nabla f \rangle_\alpha &= \frac{1}{b\delta A} \int_{\delta V} \gamma_\alpha \nabla f d\nu \\ &= \frac{1}{b} \nabla \left( \frac{1}{\delta A} \int_{\delta V} \gamma_\alpha f d\nu \right) - \frac{1}{b\delta A} \int_{\delta V} f \nabla \gamma_\alpha d\nu \end{aligned} \quad (\text{A7})$$

Gray and Lee [\[29\]](#) have shown that  $\nabla \gamma_\alpha$  is a multidimensional type of Dirac delta function. It can convert the last term on the r.h.s. of Eq. [\(A7\)](#) to the integrals over boundaries of the  $\alpha$  phase, namely,  $\sum_{\beta \neq \alpha} \delta S_{\alpha\beta}$ ,  $\delta S_\alpha^T$  and  $\delta S_\alpha^B$ . Also, with the help of Eq. [\(A3\)](#), we can obtain:

$$\langle \nabla f \rangle_\alpha = \frac{1}{b} \nabla_h (b \langle f \rangle_\alpha) + \sum_{\beta \neq \alpha} \frac{1}{b \delta A} \int_{\delta S_{\alpha\beta}} f \mathbf{n}^{\alpha\beta} d\sigma + \frac{1}{b \delta A} \int_{\delta S_\alpha^T} f \mathbf{n}^T d\sigma + \frac{1}{b \delta A} \int_{\delta S_\alpha^B} f \mathbf{n}^B d\sigma \quad (\text{A8})$$

where  $\mathbf{n}^{\alpha\beta}$  is the normal vector at the  $\alpha\beta$  interface pointing into the  $\beta$  phase,  $\mathbf{n}^T$  and  $\mathbf{n}^B$  are the outward normal vectors at the top and bottom boundaries of the porous layer, respectively. It is noted that after averaging over the REV, the gradient operator in the first term on the r.h.s of Eq. (A8) becomes 2D, because both layer thickness and  $\langle f \rangle_\alpha$  depend on the planar coordinates only.

### A.3. Temporal averaging theorem

This theorem relates the spatial average of a time derivative to the derivative of a spatial average. With the help of the chain rule, the spatial average of a time derivative in the  $\alpha$  phase is given:

$$\begin{aligned} \langle \frac{\partial f}{\partial t} \rangle_\alpha &= \frac{1}{b \delta A} \int_{\delta V} \gamma_\alpha \frac{\partial f}{\partial t} d\nu \\ &= \frac{1}{b \delta A} \int_{\delta V} \frac{\partial}{\partial t} (\gamma_\alpha f) d\nu - \frac{1}{b \delta A} \int_{\delta V} f \frac{\partial \gamma_\alpha}{\partial t} d\nu \end{aligned} \quad (\text{A9})$$

Gray and Lee [29] have shown that:

$$\frac{\partial \gamma_\alpha}{\partial t} = -\mathbf{w} \cdot \nabla \gamma_\alpha \quad (\text{A10})$$

where  $\mathbf{w}$  denotes the velocity of the  $\alpha\beta$  interface. Similar to the manipulation for the spatial averaging theorem, Eq. (A9) can be recast into:

$$\begin{aligned} \langle \frac{\partial f}{\partial t} \rangle_\alpha &= \frac{1}{b} \frac{\partial (b \langle f \rangle_\alpha)}{\partial t} - \sum_{\beta \neq \alpha} \frac{1}{b \delta A} \int_{\delta S_{\alpha\beta}} f \mathbf{w} \cdot \mathbf{n}^{\alpha\beta} d\sigma - \frac{1}{b \delta A} \int_{\delta S_\alpha^T} f \mathbf{w} \cdot \mathbf{n}^T d\sigma \\ &\quad - \frac{1}{b \delta A} \int_{\delta S_\alpha^B} f \mathbf{w} \cdot \mathbf{n}^B d\sigma \end{aligned} \quad (\text{A11})$$

Now, we average Eq. (A1) over the REV, and multiply it by  $b$  to get:

$$b \left\langle \frac{\partial (\rho \psi)}{\partial t} \right\rangle_\alpha + b \langle \nabla \cdot (\rho \mathbf{v} \psi) \rangle_\alpha - b \langle \nabla \cdot \mathbf{i} \rangle_\alpha - b \langle \rho \lambda \rangle_\alpha = b \langle \rho G \rangle_\alpha \quad (\text{A12})$$

Based on the above macroscopic definitions and the two averaging theorems, we recast Eq. (A12) into the following form:

$$\begin{aligned} \frac{\partial}{\partial t} (b e^\alpha \rho^\alpha \psi^\alpha) + \nabla_h \cdot (b e^\alpha \rho^\alpha \mathbf{v}_h^\alpha \psi^\alpha) - \nabla_h \cdot (b \mathbf{i}_h^\alpha) - b e^\alpha \rho^\alpha \lambda^\alpha \\ - b e^\alpha \rho^\alpha [b e^\alpha \rho^\alpha (\rho) + I^\alpha] = e^\alpha \rho^\alpha \left[ G^\alpha + \left( \psi^\alpha e_\alpha^T + I_\alpha^T \right) + \left( \psi^\alpha e_\alpha^B + I_\alpha^B \right) \right] \end{aligned} \quad (\text{A13})$$

where

$$\mathbf{i}_h^\alpha = \left\{ \langle \mathbf{i} \rangle_\alpha - \langle \rho \tilde{\mathbf{v}} \tilde{\psi} \rangle_\alpha \right\}_h \quad (\text{A14})$$

$$e^\alpha(\rho) = \frac{1}{b e^\alpha \rho^\alpha \delta A} \sum_{\beta \neq \alpha} \int_{\delta S_{\alpha\beta}} \rho (\mathbf{w} - \mathbf{v}) \cdot \mathbf{n}^{\alpha\beta} d\sigma \quad (\text{A15})$$

$$e_\alpha^T = \frac{1}{b e^\alpha \rho^\alpha \delta A} \int_{\delta S_\alpha^T} \rho (\mathbf{w} - \mathbf{v}) \cdot \mathbf{n}^T d\sigma \quad (\text{A16})$$

$$e_\alpha^B = \frac{1}{b e^\alpha \rho^\alpha \delta A} \int_{\delta S_\alpha^B} \rho (\mathbf{w} - \mathbf{v}) \cdot \mathbf{n}^B d\sigma \quad (\text{A17})$$

$$I^\alpha = \frac{1}{b e^\alpha \rho^\alpha \delta A} \sum_{\beta \neq \alpha} \int_{\delta S_{\alpha\beta}} [\mathbf{i} + \rho (\mathbf{w} - \mathbf{v}) \tilde{\psi}] \cdot \mathbf{n}^{\alpha\beta} d\sigma \quad (\text{A18})$$

$$I_\alpha^T = \frac{1}{b e^\alpha \rho^\alpha \delta A} \int_{\delta S_\alpha^T} [\mathbf{i} + \rho (\mathbf{w} - \mathbf{v}) \tilde{\psi}] \cdot \mathbf{n}^T d\sigma \quad (\text{A19})$$

$$I_\alpha^B = \frac{1}{b e^\alpha \rho^\alpha \delta A} \int_{\delta S_\alpha^B} [\mathbf{i} + \rho (\mathbf{w} - \mathbf{v}) \tilde{\psi}] \cdot \mathbf{n}^B d\sigma \quad (\text{A20})$$

In the above equations,  $\mathbf{i}_h^\alpha$  is the volume-averaged contact flux vector within the  $\alpha$  phase, the subscript  $h$  means that the vectorial quantity has only the in-plane components.  $\tilde{\mathbf{v}}$  and  $\tilde{\psi}$  denote the fluctuations of velocity and thermodynamic property of interest, respectively (e.g. it is defined as  $\tilde{\psi} = \psi - \psi^\alpha$ ). The quantity  $e^\alpha(\rho)$  is the mass exchange between the  $\alpha$  phase and all other phases through their interfaces,  $\sum_{\beta \neq \alpha} \delta S_{\alpha\beta}$  (see Eq. (A15)), and  $I^\alpha$  accounts for the transfer of property  $\psi$  to the  $\alpha$  phase (e.g. diffusion or mechanical interaction) in addition to  $\psi^\alpha e^\alpha(\rho)$ .  $e_\alpha^T$  and  $e_\alpha^B$  denote the  $\alpha$ -phase mass exchanges with neighboring layers on the top and bottom of the layer, respectively. Also,  $I_\alpha^T$  and  $I_\alpha^B$  account for the transfer of property  $\psi$  in addition to  $e_\alpha^T$  and  $e_\alpha^B$ , respectively. It is worth noting that by averaging over the REV, we obtain the reduced 2D balance equations with the gradient operation of  $\nabla_h$ . Finally, because of the assumption that no thermodynamic properties are stored at the phase interfaces, the exchange terms are subject to the following restriction:

$$\sum_\alpha [\psi^\alpha e^\alpha(\rho) + I^\alpha] = 0 \quad (\text{A21})$$

## Appendix B. Definition of macroscopic quantities in terms of averages of microscopic quantities

### B.1. Species mass balance

Volume-averaged nonconvective species mass flux

$$\mathbf{j}_{ih}^\alpha = \left\{ \langle \mathbf{j}_i \rangle_\alpha - \langle \rho \tilde{\mathbf{v}} \tilde{\omega}_i \rangle_\alpha \right\}_h \quad (\text{B1})$$

Diffusive flux of mass of species  $i$  into the  $\alpha$  phase

$$J_i^\alpha = \frac{1}{b e^\alpha \rho^\alpha \delta A} \sum_{\beta \neq \alpha} \int_{\delta S_{\alpha\beta}} [\mathbf{j}_i + \rho (\mathbf{w} - \mathbf{v}) \tilde{\omega}_i] \cdot \mathbf{n}^{\alpha\beta} d\sigma \quad (\text{B2})$$

Mass exchange of species  $i$  with layer  $k-1$  through the top of layer  $k$

$$J_{iz}^T = \frac{1}{b e^\alpha \rho^\alpha \delta A} \int_{\delta S_\alpha^T} [\mathbf{j}_i + \rho (\mathbf{w} - \mathbf{v}) \tilde{\omega}_i] \cdot \mathbf{n}^T d\sigma \quad (\text{B3})$$

Mass exchange of species  $i$  with layer  $k+1$  through the bottom of layer  $k$

$$J_{iz}^B = \frac{1}{b e^\alpha \rho^\alpha \delta A} \int_{\delta S_\alpha^B} [\mathbf{j}_i + \rho (\mathbf{w} - \mathbf{v}) \tilde{\omega}_i] \cdot \mathbf{n}^B d\sigma \quad (\text{B4})$$

### B.2. Momentum balance

Macroscopic stress tensor

$$\mathbf{t}_h^\alpha = \left\{ \langle \mathbf{t} \rangle_\alpha - \langle \rho \tilde{\mathbf{v}} \tilde{\nu} \rangle_\alpha \right\}_h \quad (\text{B5})$$

Momentum exchange between the  $\alpha$  phase and all other phases within the layer

$$\mathbf{T}^\alpha = \frac{1}{b e^\alpha \rho^\alpha \delta A} \sum_{\beta \neq \alpha} \int_{\delta S_{\alpha\beta}} [\mathbf{t} + \rho (\mathbf{w} - \mathbf{v}) \tilde{\nu}] \cdot \mathbf{n}^{\alpha\beta} d\sigma \quad (\text{B6})$$

Momentum exchange of the  $\alpha$  phase with layer  $k-1$  through the top of layer  $k$

$$\mathbf{T}_z^T = \frac{1}{b e^\alpha \rho^\alpha \delta A} \int_{\delta S_\alpha^T} [\mathbf{t} + \rho (\mathbf{w} - \mathbf{v}) \tilde{\nu}] \cdot \mathbf{n}^T d\sigma \quad (\text{B7})$$

Momentum exchange of the  $\alpha$  phase with layer  $k+1$  through the bottom of layer  $k$

$$\mathbf{T}_\alpha^B = \frac{1}{\varepsilon^\alpha \rho^\alpha \delta A} \int_{\delta S_\alpha^B} [\mathbf{t} + \rho(\mathbf{w} - \mathbf{v})\tilde{\mathbf{v}}] \cdot \mathbf{n}^B d\sigma \quad (\text{B8})$$

### B.3. Energy balance

Macroscopic heat flux

$$\mathbf{q}_h^\alpha = \left\{ \langle \mathbf{q} \rangle_\alpha + \langle \mathbf{t} \cdot \tilde{\mathbf{v}} \rangle_\alpha - \langle \rho \tilde{\mathbf{v}} E \rangle_\alpha - \frac{1}{2} \langle \rho \tilde{\mathbf{v}} \tilde{v}^2 \rangle_\alpha \right\}_h \quad (\text{B9})$$

Energy exchange between the  $\alpha$  phase and all other phases

$$Q^\alpha = \frac{1}{b \varepsilon^\alpha \rho^\alpha \delta A} \sum_{\beta \neq \alpha} \int_{\delta S_{\alpha\beta}} \left[ (\mathbf{t} \cdot \tilde{\mathbf{v}} + \mathbf{q}) + \rho(\mathbf{w} - \mathbf{v}) \left( E + \frac{1}{2} \tilde{v}^2 - E^\alpha \right) \right] \cdot \mathbf{n}^{\alpha\beta} d\sigma \quad (\text{B10})$$

Energy exchange of the  $\alpha$  phase with layer  $k-1$  through the top of layer  $k$

$$Q_\alpha^T = \frac{1}{\varepsilon^\alpha \rho^\alpha \delta A} \int_{\delta S_\alpha^T} \left[ (\mathbf{t} \cdot \tilde{\mathbf{v}} + \mathbf{q}) + \rho(\mathbf{w} - \mathbf{v}) \left( E + \frac{1}{2} \tilde{v}^2 - E^\alpha \right) \right] \cdot \mathbf{n}^T d\sigma \quad (\text{B11})$$

Energy exchange of the  $\alpha$  phase with layer  $k+1$  through the bottom of layer  $k$

$$Q_\alpha^B = \frac{1}{\varepsilon^\alpha \rho^\alpha \delta A} \int_{\delta S_\alpha^B} \left[ (\mathbf{t} \cdot \tilde{\mathbf{v}} + \mathbf{q}) + \rho(\mathbf{w} - \mathbf{v}) \left( E + \frac{1}{2} \tilde{v}^2 - E^\alpha \right) \right] \cdot \mathbf{n}^B d\sigma \quad (\text{B12})$$

### B.4. Entropy balance

Macroscopic entropy flux

$$\psi_h^\alpha = \left\{ \langle \psi \rangle_\alpha - \langle \rho \tilde{\mathbf{v}} \tilde{S} \rangle_\alpha \right\}_h \quad (\text{B13})$$

Entropy exchange between the  $\alpha$  phase and all other phases

$$\Phi^\alpha = \frac{1}{b \varepsilon^\alpha \rho^\alpha \delta A} \sum_{\alpha \neq \beta} \int_{\delta S_{\alpha\beta}} [\psi + \rho(\mathbf{w} - \mathbf{v})\tilde{S}] \cdot \mathbf{n}^{\alpha\beta} d\sigma \quad (\text{B14})$$

Entropy exchange of the  $\alpha$  phase with layer  $k-1$  through the top of layer  $k$

$$\Phi_\alpha^T = \frac{1}{\varepsilon^\alpha \rho^\alpha \delta A} \int_{\delta S_\alpha^T} [\psi + \rho(\mathbf{w} - \mathbf{v})\tilde{S}] \cdot \mathbf{n}^T d\sigma \quad (\text{B15})$$

Entropy exchange of the  $\alpha$  phase with layer  $k+1$  through the bottom of layer  $k$

$$\Phi_\alpha^B = \frac{1}{\varepsilon^\alpha \rho^\alpha \delta A} \int_{\delta S_\alpha^B} [\psi + \rho(\mathbf{w} - \mathbf{v})\tilde{S}] \cdot \mathbf{n}^B d\sigma \quad (\text{B16})$$

### Appendix C. Exploitation of the entropy inequality

The axiom of admissibility states that “the set of constitutive equations for dependent variables must not be in contradiction with the second law of thermodynamics and balance laws”. We obtained Eq. (34) by the combination of balance equations of mass, momentum, energy, and entropy, and the restrictions at the phase interfaces. Therefore, when constitutive assumptions are substituted into Eq. (34), the entropy inequality must be valid for

all possible thermodynamic processes. This requirement would help us select proper constitutive equations. Now, we explore the expansion form of the second law of thermodynamics by the method of Coleman and Noll [15].

First, based on the assumptions (Eqs. (35), (36) and (43)), and with the help of the continuity conditions at the layer-layer boundary (listed in Table 2), we recast Eq. (34) into the following form:

$$\begin{aligned} \Lambda = & \sum_{k=1}^2 \sum_{\alpha} b \varepsilon^\alpha \rho^\alpha \Gamma^\alpha \Big|_k = - \sum_{k=1}^2 \sum_{\alpha} \frac{b \varepsilon^\alpha \rho^\alpha}{\theta} \left( \frac{D_h^\alpha A^\alpha}{Dt} + S^\alpha \frac{D_h^\alpha \theta}{Dt} \right) \Big|_k \\ & + \sum_{k=1}^2 \sum_{\alpha} \frac{b}{\theta} \mathbf{t}_h^\alpha : \nabla_h \mathbf{v}^\alpha \Big|_k + \sum_{k=1}^2 \sum_{\alpha} \frac{b \mathbf{q}_h^\alpha \cdot \nabla_h \theta}{\theta^2} \Big|_k \\ & - \sum_{k=1}^2 \sum_{\alpha \neq s} \frac{b \varepsilon^\alpha \rho^\alpha}{\theta^r} \mathbf{T}^\alpha \cdot \mathbf{v}^{\alpha,s} \Big|_k - \frac{\theta^{1,r}}{\theta_1 \theta^r} \sum_{\alpha} (b \varepsilon^\alpha \rho^\alpha Q^\alpha) \Big|_1 \\ & - \frac{\theta^{2,r}}{\theta_2 \theta^r} \sum_{\alpha} (b \varepsilon^\alpha \rho^\alpha Q^\alpha) \Big|_2 + \sum_{\alpha} (\varepsilon^\alpha \rho^\alpha e_\alpha^B) \Big|_1 \left( \frac{A_2^\alpha}{\theta_2} - \frac{A_1^\alpha}{\theta_1} \right) \\ & - \frac{\theta^{1,r}}{\theta_1 \theta^r} \sum_{\alpha} \left[ \varepsilon^\alpha \rho^\alpha (e_\alpha^B E^\alpha + Q_\alpha^B) \right] \Big|_1 - \frac{\theta^{2,r}}{\theta_2 \theta^r} \sum_{\alpha} \left[ \varepsilon^\alpha \rho^\alpha (e_\alpha^T E^\alpha + Q_\alpha^T) \right] \Big|_2 \\ & + \sum_{\alpha \neq s} \frac{(\varepsilon^\alpha \rho^\alpha e_\alpha^B) \Big|_1}{\theta^r} \left[ \frac{1}{2} (v_2^{\alpha,s})^2 - \frac{1}{2} (v_1^{\alpha,s})^2 \right] - \sum_{\alpha \neq s} \frac{\varepsilon^\alpha \rho^\alpha}{\theta^r} \mathbf{T}_\alpha^s \cdot \mathbf{v}^{\alpha,s} \Big|_2 \\ & - \sum_{\alpha \neq s} \frac{\varepsilon^\alpha \rho^\alpha}{\theta^r} \mathbf{T}_\alpha^s \cdot \mathbf{v}^{\alpha,s} \Big|_2 \\ & + \underbrace{\left( \sum_{\alpha} \frac{\varepsilon^\alpha \rho^\alpha}{\theta_1} Q_\alpha^T \Big|_1 + \sum_{\alpha} \frac{\varepsilon^\alpha \rho^\alpha}{\theta_2} Q_\alpha^B \Big|_2 - \sum_{\alpha} \varepsilon^\alpha \rho^\alpha \Phi_\alpha^T \Big|_1 - \sum_{\alpha} \varepsilon^\alpha \rho^\alpha \Phi_\alpha^B \Big|_2 \right)}_{\text{Boundary conditions}} \geq 0 \end{aligned} \quad (\text{C1})$$

where the numeral subscript associated with the quantities denotes the layer index (1 or 2), the subscript behind a vertical bar also denotes the layer index. Note that in obtaining the above form of entropy inequality (C1), the solid phase velocity in either layer is taken as the reference velocity.

Then, by means of chain rule, we expand the derivatives of the free energy functions (Eqs. (44) and (45)) to be:

$$\frac{D_h^\alpha A^\alpha}{Dt} \Big|_k = \left( \frac{\partial A^\alpha}{\partial \rho^\alpha} \frac{D_h^\alpha \rho^\alpha}{Dt} + \frac{\partial A^\alpha}{\partial S^\alpha} \frac{D_h^\alpha S^\alpha}{Dt} + \frac{\partial A^\alpha}{\partial \theta} \frac{D_h^\alpha \theta}{Dt} + \frac{\partial A^\alpha}{\partial b} \frac{D_h^\alpha b}{Dt} \right) \Big|_k \quad \alpha = g, l \quad (\text{C2})$$

$$\frac{D_h^s A^s}{Dt} \Big|_k = \left( \frac{\partial A^s}{\partial \rho^s} \frac{D_h^s \rho^s}{Dt} + \frac{\partial A^s}{\partial S^s} \frac{D_h^s S^s}{Dt} + \frac{\partial A^s}{\partial \theta} \frac{D_h^s \theta}{Dt} + \frac{\partial A^s}{\partial b} \frac{D_h^s b}{Dt} + \frac{\partial A^s}{\partial E^s} \frac{D_h^s E^s}{Dt} \right) \Big|_k \quad (\text{C3})$$

Also, the mass conservation equation, Eq. (11), is used to evaluate  $D_h^\alpha \rho^\alpha / Dt$  to be:

$$\frac{D_h^\alpha \rho^\alpha}{Dt} \Big|_k = \left[ \frac{\rho^\alpha}{b} (e_\alpha^T + e_\alpha^B) - \frac{\rho^\alpha}{\varepsilon^\alpha} \frac{D_h^\alpha \varepsilon^\alpha}{Dt} - \frac{\rho^\alpha}{b} \frac{D_h^\alpha b}{Dt} - \rho^\alpha \nabla_h \cdot \mathbf{v}_h^\alpha \right] \Big|_k \quad \alpha = g, l \quad (\text{C4})$$

$$\frac{D_h^s \rho^s}{Dt} \Big|_k = \left[ \frac{\rho^s}{b} (e_s^T + e_s^B) - \frac{\rho^s}{\varepsilon^s} \frac{D_h^s \varepsilon^s}{Dt} - \frac{\rho^s}{b} \frac{D_h^s b}{Dt} - \rho^s \nabla_h \cdot \mathbf{v}_h^s \right] \Big|_k \quad (\text{C5})$$

Finally, substitution of Eqs. C2, C3, C4, C5 into Eq. (C1), and after much tedious manipulation and algebra, yield the final expanding form of the entropy inequality as:

$$\begin{aligned}
\Lambda = & \sum_{k=1}^2 \sum_{\alpha} b \epsilon^{\alpha} \rho^{\alpha} \Gamma^{\alpha} \Big|_k \\
= & - \sum_{k=1}^2 \frac{D_h^s \theta}{Dt} \left[ \sum_{\alpha \neq s} \frac{b \epsilon s^{\alpha} \rho^{\alpha}}{\theta} \left( \frac{\partial A^{\alpha}}{\partial \theta} + S^{\alpha} \right) + \frac{b(1-\epsilon) \rho^s}{\theta} \left( \frac{\partial A^s}{\partial \theta} + S^s \right) \right] \Big|_k + \sum_{k=1}^2 \sum_{\alpha \neq s} \mathbf{d}^{\alpha} : \frac{b}{\theta} \left( \mathbf{t}^{\alpha} + \epsilon s^{\alpha} (\rho^{\alpha})^2 \frac{\partial A^{\alpha}}{\partial \rho^{\alpha}} \mathbf{I} \right) \Big|_k \\
& + \sum_{k=1}^2 \mathbf{d}^s : \frac{b}{\theta} \left[ \mathbf{t}^s + (1-\epsilon) (\rho^s)^2 \frac{\partial A^s}{\partial \rho^s} \mathbf{I} - (1-\epsilon) \rho^s (\text{GRAD} \mathbf{F}_h^s)^T \cdot \frac{\partial A^s}{\partial \mathbf{E}^s} \cdot (\text{GRAD} \mathbf{F}_h^s) \right] \Big|_k + \sum_{k=1}^2 \frac{D_h^s \epsilon}{Dt} \left[ \sum_{\alpha \neq s} \frac{b}{\theta} (\rho^{\alpha})^2 \frac{\partial A^{\alpha}}{\partial \rho^{\alpha}} S^{\alpha} - \frac{b}{\theta} (\rho^s)^2 \frac{\partial A^s}{\partial \rho^s} \right] \Big|_k \\
& + \sum_{k=1}^2 \frac{D_h^s S^s}{Dt} \left[ \frac{b \epsilon s^g \rho^g}{\theta} \frac{\partial A^g}{\partial S^g} - \frac{b \epsilon s^l \rho^l}{\theta} \frac{\partial A^l}{\partial S^l} - \frac{b(1-\epsilon) \rho^s}{\theta} \frac{\partial A^s}{\partial S^s} + \frac{b \epsilon}{\theta} (\rho^s)^2 \frac{\partial A^l}{\partial \rho^l} - \frac{b \epsilon}{\theta} (\rho^s)^2 \frac{\partial A^g}{\partial \rho^g} \right] \Big|_k \\
& + \sum_{k=1}^2 \frac{D_h^s b}{Dt} \left[ \frac{(1-\epsilon) (\rho^s)^2}{\theta} \frac{\partial A^s}{\partial \rho^s} - \frac{b(1-\epsilon) \rho^s}{\theta} \frac{\partial A^s}{\partial b} + \sum_{\alpha \neq s} \left( \frac{\epsilon s^{\alpha} (\rho^{\alpha})^2}{\theta} \frac{\partial A^{\alpha}}{\partial \rho^{\alpha}} - \frac{b \epsilon s^{\alpha} \rho^{\alpha}}{\theta} \frac{\partial A^{\alpha}}{\partial b} \right) \right] \Big|_k \\
& + \sum_{\alpha \neq s} \mathbf{v}_h^{\alpha, s} \cdot \left\{ \left[ \frac{\epsilon s^{\alpha} (\rho^{\alpha})^2}{\theta_1} \frac{\partial A^{\alpha}}{\partial \rho^{\alpha}} - \frac{b \epsilon s^{\alpha} \rho^{\alpha}}{\theta_1} \frac{\partial A^{\alpha}}{\partial b} \right] \nabla_h b + \frac{b (\rho^{\alpha})^2}{\theta_1} \frac{\partial A^{\alpha}}{\partial \rho^{\alpha}} \nabla_h (\epsilon s^{\alpha}) - \frac{b \epsilon s^{\alpha} \rho^{\alpha}}{\theta_1} \frac{\partial A^{\alpha}}{\partial S^{\alpha}} \nabla_h S^{\alpha} - \frac{b \epsilon s^{\alpha} \rho^{\alpha}}{\theta^r} \mathbf{T}_h^{\alpha} - \frac{\epsilon s^{\alpha} \rho^{\alpha} \mathbf{T}_{h\alpha}^B}{\theta^r} \right\}_1 \\
& + \sum_{\alpha \neq s} \mathbf{v}_h^{\alpha, s} \cdot \left\{ \left[ \frac{\epsilon s^{\alpha} (\rho^{\alpha})^2}{\theta_2} \frac{\partial A^{\alpha}}{\partial \rho^{\alpha}} - \frac{b \epsilon s^{\alpha} \rho^{\alpha}}{\theta_2} \frac{\partial A^{\alpha}}{\partial b} \right] \nabla_h b + \frac{b (\rho^{\alpha})^2}{\theta_2} \frac{\partial A^{\alpha}}{\partial \rho^{\alpha}} \nabla_h (\epsilon s^{\alpha}) - \frac{b \epsilon s^{\alpha} \rho^{\alpha}}{\theta_2} \frac{\partial A^{\alpha}}{\partial S^{\alpha}} \nabla_h S^{\alpha} - \frac{b \epsilon s^{\alpha} \rho^{\alpha}}{\theta^r} \mathbf{T}_h^{\alpha} - \frac{\epsilon s^{\alpha} \rho^{\alpha} \mathbf{T}_{h\alpha}^T}{\theta^r} \right\}_2 \\
& - \sum_{\alpha \neq s} \mathbf{v}_v^{\alpha, s} \left( \frac{b \epsilon s^{\alpha} \rho^{\alpha}}{\theta^r} T_v^{\alpha} + \frac{\epsilon s^{\alpha} \rho^{\alpha} T_{v\alpha}^B}{\theta^r} \right) \Big|_1 - \sum_{\alpha \neq s} \mathbf{v}_v^{\alpha, s} \left( \frac{b \epsilon s^{\alpha} \rho^{\alpha}}{\theta^r} T_v^{\alpha} + \frac{\epsilon s^{\alpha} \rho^{\alpha} T_{v\alpha}^T}{\theta^r} \right) \Big|_2 \\
& + \sum_{\alpha} \mathbf{e}_x^B \Big|_1 \left\{ \frac{\epsilon_1^2 \rho_1^{\alpha} \rho_2^{\alpha}}{\theta_2} \frac{\partial A_2^{\alpha}}{\partial \rho_2^{\alpha}} - \frac{\epsilon_1^2 (\rho_1^{\alpha})^2}{\theta_1} \frac{\partial A_1^{\alpha}}{\partial \rho_1^{\alpha}} + \epsilon_1^2 \rho_1^{\alpha} \left( \frac{A_2^{\alpha}}{\theta_2} - \frac{A_1^{\alpha}}{\theta_1} \right) + \frac{\epsilon_1^2 \rho_1^{\alpha}}{\theta^r} \left[ \frac{1}{2} (\nu_2^{\alpha, s})^2 - \frac{1}{2} (\nu_1^{\alpha, s})^2 \right] + \frac{\theta^{2, r}}{\theta_2 \theta^r} \epsilon_1^2 \rho_1^{\alpha} E_2^{\alpha} - \frac{\theta^{1, r}}{\theta_1 \theta^r} \epsilon_1^2 \rho_1^{\alpha} E_1^{\alpha} \right\} \\
& + \sum_{k=1}^2 \sum_{\alpha} \frac{b \mathbf{q}_h^{\alpha}}{(\theta)^2} \cdot \nabla_h \theta \Big|_k - \sum_{k=1}^2 \sum_{\alpha \neq s} \frac{b \epsilon s^{\alpha} \rho^{\alpha}}{\theta} \left( \frac{\partial A^{\alpha}}{\partial \theta} + S^{\alpha} \right) \mathbf{v}^{\alpha, s} \cdot \nabla_h \theta \Big|_k - \frac{\theta^{1, r}}{\theta_1 \theta^r} \left( \sum_{\alpha} b \epsilon^{\alpha} \rho^{\alpha} Q^{\alpha} \Big|_1 + \sum_{\alpha} \epsilon^{\alpha} \rho^{\alpha} Q_x^B \Big|_1 \right) - \frac{\theta^{2, r}}{\theta_2 \theta^r} \left( \sum_{\alpha} b \epsilon^{\alpha} \rho^{\alpha} Q^{\alpha} \Big|_2 + \sum_{\alpha} \epsilon^{\alpha} \rho^{\alpha} Q_x^T \Big|_2 \right) \\
& + \left( \sum_{\alpha} \frac{\epsilon^{\alpha} \rho^{\alpha}}{\theta_1} Q_x^T \Big|_1 + \sum_{\alpha} \frac{\epsilon^{\alpha} \rho^{\alpha}}{\theta_2} Q_x^B \Big|_2 - \sum_{\alpha} \epsilon^{\alpha} \rho^{\alpha} \Phi_x^T \Big|_1 - \sum_{\alpha} \epsilon^{\alpha} \rho^{\alpha} \Phi_x^B \Big|_2 \right) - \sum_{\alpha} \frac{\epsilon_1^2 (\rho_1^{\alpha})^2}{\theta_1} \frac{\partial A_1^{\alpha}}{\partial \rho_1^{\alpha}} e_x^T \Big|_1 - \sum_{\alpha} \frac{\epsilon_2^2 (\rho_2^{\alpha})^2}{\theta_2} \frac{\partial A_2^{\alpha}}{\partial \rho_2^{\alpha}} e_x^B \Big|_2 \geq 0
\end{aligned} \tag{C6}$$

Boundary conditions

In Eq. (C6),  $\mathbf{d}^{\alpha}$  is the planar deformation rate tensor (Eq. (9)).  $\mathbf{I}$  is the identity tensor ( $2 \times 2$ ). The subscript  $h\alpha$  denotes the planar part (in the in-plane directions) of the quantity in the  $\alpha$  phase, while the subscript  $v\alpha$  denotes the vertical component (in the through-plane direction) of the quantity in the  $\alpha$  phase. The last grouped several terms are given by boundary conditions. They account for the entropy production due to the addition and removal of heat and mass through the top of layer 1 and the bottom of layer 2. These terms must be greater than or equal to zero. The functional forms of the other terms in Eq. (C6) do not depend on the boundary conditions. Thus, the entropy inequality must be satisfied even when the last grouped terms are neglected. In further discussion of the entropy inequality, omission of these terms should be reasonable.

In the first three terms on the l.h.s. of Eq. (C6), the variables  $D_h^s \theta / Dt$ ,  $\mathbf{d}^{\alpha} (\alpha \neq s)$ , and  $\mathbf{d}^s$  appear linearly, because none of the constitutive functions are assumed to depend on these variables. The necessary and sufficient condition for the inequality to be valid for all thermodynamic states is that the coefficients of the above mentioned variables must vanish. This would lead to the following relationships:

$$\left[ \sum_{\alpha \neq s} \frac{b \epsilon s^{\alpha} \rho^{\alpha}}{\theta} \left( \frac{\partial A^{\alpha}}{\partial \theta} + S^{\alpha} \right) + \frac{b(1-\epsilon) \rho^s}{\theta} \left( \frac{\partial A^s}{\partial \theta} + S^s \right) \right]_k = 0 \quad \alpha = g, l \tag{C7}$$

$$\mathbf{t}^{\alpha} \Big|_k = -(\epsilon s^{\alpha} \rho^{\alpha} \mathbf{I}) \Big|_k \quad \alpha = g, l \tag{C8}$$

$$\mathbf{t}^s \Big|_k = - \left[ (1-\epsilon) \rho^s \mathbf{I} - (1-\epsilon) \rho^s (\text{GRAD} \mathbf{F}_h^s)^T \cdot \frac{\partial A^s}{\partial \mathbf{E}^s} \cdot (\text{GRAD} \mathbf{F}_h^s) \right] \Big|_k \tag{C9}$$

Here,  $\rho^{\alpha}$  is the thermodynamic definition of the phase pressure, given by:

$$\rho^{\alpha} \Big|_k = (\rho^{\alpha})^2 \frac{\partial A^{\alpha}}{\partial \rho^{\alpha}} \Big|_k \tag{C10}$$

After the above operation and dropping the boundary contributions, the entropy inequality (C6) reduces to the form of (46).

#### Appendix D. Simplification of mass exchange term between two neighboring layers

According to linearization theory, we obtain the mass exchange term as:

$$\epsilon_1^2 \rho_1^{\alpha} e_x^B \Big|_1 = \Pi_m \left\{ \left( \frac{G_2^{\alpha}}{\theta_2} - \frac{G_1^{\alpha}}{\theta_1} \right) + \frac{1}{\theta^r} \left[ \frac{1}{2} (\nu_2^{\alpha, s})^2 - \frac{1}{2} (\nu_1^{\alpha, s})^2 \right] + \frac{\theta^{2, r}}{\theta_2 \theta^r} E_2^{\alpha} - \frac{\theta^{1, r}}{\theta_1 \theta^r} E_1^{\alpha} \right\} \tag{D1}$$

Substitution of Eq. (56) into Eq. (D1), and after some algebra yield:

$$\begin{aligned}
\epsilon_1^2 \rho_1^{\alpha} e_x^B \Big|_1 &= \Pi_m \left\{ \left( \frac{p_2^{\alpha}}{\theta_2 \rho_2^{\alpha}} - \frac{p_1^{\alpha}}{\theta_1 \rho_1^{\alpha}} \right) + \frac{1}{\theta^r} \left[ \frac{1}{2} (\nu_2^{\alpha, s})^2 - \frac{1}{2} (\nu_1^{\alpha, s})^2 \right] \right. \\
&\quad \left. + \frac{1}{\theta^r} (E_2^{\alpha} - E_1^{\alpha}) - (S_2^{\alpha} - S_1^{\alpha}) \right\}
\end{aligned} \tag{D2}$$

Previous work [22] suggested that inside a phase, the derivative of Helmholtz free energy with respect to the phase temperature is opposite to the entropy:

$$\frac{\partial A^{\alpha}}{\partial \theta^{\alpha}} = -S^{\alpha} \tag{D3}$$

Still according to the definition of Gibbs free energy (Eq. (56)), Eq. (D3) can be rearranged to be:

$$\frac{\partial E}{\partial S} = \theta \tag{D4}$$

If we can approximate the differential of some quantity by the difference in the two layers and take  $\theta = \theta^r$ , Eq. (D4) becomes:

$$\frac{1}{\theta^r} (E_2^x - E_1^x) - (S_2^x - S_1^x) = 0 \quad (\text{D5})$$

Finally, if we consider slow flow in thin porous layers (for instance, in PEFC application, water velocity is on the order of  $10^{-4}$ ), the driving force coming from the difference in kinetic energies can be neglected. Also with the help of Eq. (D5), we can reduce the mass exchange term to the following form:

$$\epsilon_1^x \rho_1^x e_1^B |_1 = \Pi_m \left( \frac{p_2^x}{\theta_2 \rho_2^x} - \frac{p_1^x}{\theta_1 \rho_1^x} \right) \quad (\text{D6})$$

It is found that the driving force for mass exchange between two neighboring layers is dominated by the difference in temperature-weighted fluid pressures.

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