

# Two-phase flow equations in porous media for PEMFC (Proton Exchange Membrane Fuel Cells)

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**Abstract.** In Proton Exchange Membrane Fuel Cells (PEMFC) for electrical mobility, the water management and transport are very important. Water vapour is produced, and liquid water can be formed since the gases can become saturated by water vapour production during the electrochemical reactions. In addition, significant water transport mechanisms occur between the anode and the cathode. Therefore, a two-phase flow must be considered on both sides, the two phases being the liquid water and the gas mixture (the different gas components are essentially hydrogen, oxygen, nitrogen, and water vapour). The core of a PEMFC consists of several porous media called GDL (Gas Diffusion Layer), MPL (Micro Porous Layer), and CL (Catalytic Layer). Therefore, we have a two-phase multicomponent gas-liquid flow in porous media. The objective of this paper is to present a complete derivation of the balance equations governing this kind of flow and to compare these equations to the equations used in PEMFC calculations in order to put in evidence the simplifying assumptions made by the PEMFC community.

**Keywords:** PEMFC, Porous, Two-phase, Multiconstituent, Equations, Hydrogen.

## 1 Introduction

Global warming is one of the major concerns since the beginning of this century. Climate change is primarily caused by human activity, and in particular by the transport sector, which emits large amounts of greenhouse gases. Electric cars are currently designed for emission-free modes of transport. However, electricity cannot be stored in great quantities, and its direct use through battery-powered vehicles has some limitations in terms of autonomy and recharging times. Hydrogen appears to be a viable solution for producing electricity in cars by using fuel cells. Among the different available technologies, the Proton Exchange Membrane Fuel Cell (PEMFC) seems to be the best solution for automotive applications due to its excellent dynamics, high power density, and good efficiency ( $>0.5$ ). PEMFC converts hydrogen into electrical energy when the hydrogen reacts with the oxygen in the air to produce water and energy (electricity, but also heat). Although promising, PEMFC faces challenges for their large-scale commercialisation. Their durability appears to be the main issue to be solved. Degradations, which can be irreversible, are the origin of the limited lifespan of PEMFC. These

degradations occur notably during an imperfect management of water and heat.

Due to their importance in PEMFC models, the balance equations of mass, momentum, and energy are derived in order to compare these equations with the models currently used in PEMFC simulations. We are concerned with two-phase multicomponent flows in porous media. The liquid water is a single component, but the gas phase mixture includes at least hydrogen, oxygen, nitrogen, and water vapour. The porous media involved in a PEMFC are the gas diffusion layer (GDL), the microporous layer (MPL), and the catalyst layer (CL). Sometimes, the bipolar plates (BPs) containing the gas distribution and water evacuation channels are also considered as porous media since these BPs contain a large number of small channels. After a brief literature survey (Sect. 2), Sections 3–5 give a complete derivation of the equations governing two-phase multicomponent flows in porous media. Section 3 presents the mathematical tools used in the paper as well as the local instantaneous balance equations. In Section 4, a volume averaging operator is applied to the balance equations derived in Section 3 in order to obtain their averaged counterparts. In Section 5, we give more usable forms of these equations, and Section 6 presents simplifications currently used in PEMFC models.

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## 2 Brief literature survey on the models of flows in general porous media

When studying two-phase flows in porous media, a volume averaging is generally done on a representative elementary volume (REV) containing the three phases (gas, liquid, and the solid medium) (Fig. 1). In Figure 1, Agl denotes the gas-liquid interface, Ags denotes the gas-solid interface, and Als denotes the liquid-solid interface, respectively.

Gray *et al.* [1] give the proof of general theorems relating spatial averages of derivatives to the derivatives of spatial averages for a two-phase medium (*e.g.* a porous structure embedded in a fluid). Slattery [2] considers simplified averaged mass and momentum equations for flows of viscoelastic fluids in porous media. Whitaker [3] studied the diffusion of a passive species concentration  $c$  in a porous medium. He shows that the average of the species concentration balance equation:

$$\frac{\partial \bar{c}}{\partial t} + \nabla \cdot (\underline{v}c) = \nabla \cdot (D\nabla c) \quad (1)$$

where  $\underline{v}$  is the fluid velocity and  $D$  is the molecular diffusion coefficient, is given by the following equation:

$$\frac{\partial \bar{c}}{\partial t} + \nabla \cdot (\underline{v}\bar{c} + \underline{\psi}) = \nabla \cdot (D(\nabla \bar{c} + R\underline{\tau})) \quad (2)$$

where the overbar denotes the spatial averaging operator, and the new terms  $\underline{\psi}$  and  $R\underline{\tau}$  are defined through the following equations. The vector  $\underline{\psi}$  is due to the covariance between the velocity and concentration fluctuations:

$$\underline{\psi} \stackrel{\text{def}}{=} \overline{\underline{v}'c'} \quad (3)$$

where the primed quantities represent fluctuations.  $R$  denotes the volumetric interfacial area of the porous medium and the vector  $\underline{\tau}$  is linked to the medium tortuosity. The last term in equation (2) is a reduction of the concentration diffusion if the porous medium is tortuous (*i.e.*, the links between the pores are not rectilinear). They are defined by:

$$R \stackrel{\text{def}}{=} \frac{A_i}{V} \quad \underline{\tau} \stackrel{\text{def}}{=} \int_{A_i} [c]\underline{n} da \quad (4)$$

where the non-dimensional area element  $da = dA/A_i$  and  $[c]$  is the jump of  $c$  between the fluid and solid phases at the fluid-solid interface. Other equations are written by the author for other quantities like the fluctuations  $c'$  and  $\underline{v}'$ . The remainder of his paper is a tentative model for the modelling of these unknown terms.

Abriola *et al.* [4] write several mass balance equations for a four-phase two-component medium (insertion of a pollutant in a soil containing also water and air). Except for the mass balance equations, these authors use a very simplified form of the momentum equations, which is a generalized Darcy's law for multiphase flows:

$$\underline{v}^\alpha = -\frac{KK_{r\alpha}}{\varepsilon s_\alpha \mu_\alpha} (\nabla P^\alpha - \rho^\alpha \underline{g}) \quad (5)$$

which gives the velocity of the  $\alpha$ -phase  $\underline{v}^\alpha$  as a function of the medium permeability  $K$ , the relative permeability  $K_{r\alpha}$ ,

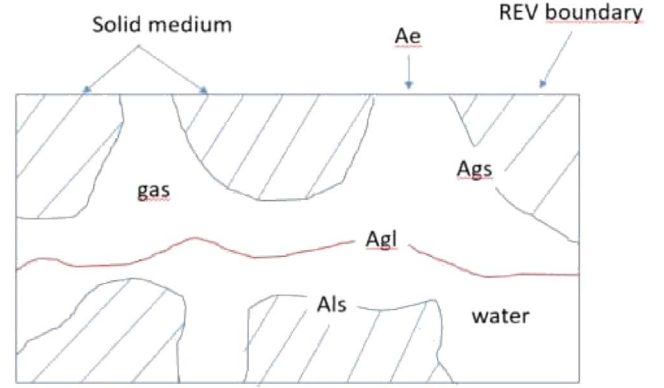


Figure 1. Scheme of a typical REV containing the three phases.

the porosity  $\varepsilon$ , the saturation  $s_\alpha$  (which is the volumetric fraction of this phase), the viscosity  $\mu_\alpha$ , the pressure gradient  $\nabla P^\alpha$ , and the gravitational acceleration vector  $\underline{g}$ . The relative permeability is often modelled as a function of the phase saturation.

In their book about convection in porous media, Nield and Bejan [5] synthesize the following mass and momentum equations for a single-phase flow in a porous medium:

$$\varepsilon \frac{\partial \rho_f}{\partial t} + \nabla \cdot (\rho_f \underline{v}) = 0 \quad (6)$$

for the mass balance equation, where  $\varepsilon$  is the porosity (ratio of the fluid volume divided by the total volume),  $\rho_f$  is the fluid density and  $\underline{v}$  is the seepage velocity, also known as the superficial velocity. It is not the real velocity but the product of it by the porosity:

$$\underline{v} = \varepsilon \underline{v}_f. \quad (7)$$

The general momentum equation reads:

$$\rho_f \left[ \frac{1}{\varepsilon} \frac{\partial \underline{v}}{\partial t} + \frac{1}{\varepsilon} \nabla \cdot \left( \frac{\underline{v}\underline{v}}{\varepsilon} \right) \right] = -\nabla p - \frac{\mu \underline{v}}{K} - c_F \frac{\rho_f}{\sqrt{K}} |\underline{v}| \underline{v} + \frac{\mu}{\varepsilon} \nabla^2 \underline{v}. \quad (8)$$

The LHS (Left Hand Side) of equation (8) is the inertial terms, and the terms on the RHS (Right Hand Side) are the pressure gradient, the friction term due to Darcy, an additional quadratic friction term due to Forchheimer, and a diffusion term due to Brinkman. equation (8) is rarely used entirely, but parts of it are supposed to balance, the other terms being neglected. We can therefore retrieve the original Darcy equation, or the Brinkman or Forchheimer equations from (8) by neglecting the appropriate terms.

Nield and Bejan [5] also introduce two thermal equations for the fluid and solid phases of the porous medium. This model is sometimes called the Local Thermal Non-Equilibrium (LTNE) since each phase is characterized by its own temperature equation, therefore taking the thermal imbalance between phases into account. The equations given by [5] read:

$$(1 - \varepsilon)(\rho c)_s \frac{\partial T_s}{\partial t} = (1 - \varepsilon) \nabla \cdot (k_s \nabla T_s) + (1 - \varepsilon) q''_s + ha(T_f - T_s) \quad (9)$$

$$\varepsilon(\rho c_p)_f \frac{\partial T_f}{\partial t} + (\rho c_p)_f \underline{v} \cdot \nabla T_f = \varepsilon \nabla \cdot (k_f \nabla T_f) + \varepsilon q''_f + ha(T_s - T_f). \quad (10)$$

In these equations,  $T_s$  and  $T_f$  denote the average solid and fluid temperatures, respectively. The quantities  $q''_s$  and  $q''_f$  denote volumetric source terms in each phase and  $h$  and  $a$  denote a heat exchange coefficient and the volumetric contact area between phases, respectively. If we assume that these two temperatures are equal:

$$T_s = T_f = T \text{ thermal equilibrium assumption} \quad (11)$$

we can deduce a single equation for the mean temperature  $T$  by adding together the two equations (9) and (10). We thus obtain:

$$(\rho c)_m \frac{\partial T}{\partial t} + (\rho c_p)_f \underline{v} \cdot \nabla T = \nabla \cdot (k_m \nabla T) + q''_m \quad (12)$$

where  $(\rho c)_m$ ,  $k_m$ , and  $q''_m$  are the physical properties of the medium and the volumetric source term in the medium, which are defined by the following equations:

$$(\rho c)_m = (1 - \varepsilon)(\rho c)_s + \varepsilon(\rho c_p)_f \quad (13)$$

$$k_m = (1 - \varepsilon)k_s + \varepsilon k_f \quad (14)$$

$$q''_m = (1 - \varepsilon)q''_s + \varepsilon q''_f. \quad (15)$$

We insist on the fact that the equations (12)–(15) are only valid under the thermal equilibrium assumption (11) and that the porosity  $\varepsilon$  should be constant in space, otherwise it cannot be excluded from the divergences as in equations (9) and (10) as we will show later.

References [6–9] derived complete set of equations for two-phase flow modelling. Their equations are very detailed, unfortunately they do not deal with porous media.

Sha *et al.* [10] started from a result demonstrated by [1]:

$$\nabla \cdot \langle \underline{\varphi}_k \rangle = \frac{1}{V} \int_{A_e} \underline{\varphi}_k \cdot \underline{n}_k \, da \quad (16)$$

where  $\underline{\varphi}_k$  is an arbitrary vector characterizing the  $k$  phase,  $\langle \underline{\varphi}_k \rangle$  is its average over the REV (Fig. 1) denoted by  $V$  and  $A_e$  is the part of  $A$  (the boundary surface of  $V$ ) available to the fluid passage (*i.e.*, the portion of  $A$  not contained in the solid parts of the medium). The relation demonstrated by [10] reads:

$$\begin{aligned} \nabla \cdot \langle \underline{\varphi}_k \rangle &= \frac{\partial}{\partial x} (\gamma_{Ax} \alpha_k \langle \varphi_{kx} \rangle_{kx}) + \frac{\partial}{\partial y} (\gamma_{Ay} \alpha_k \langle \varphi_{ky} \rangle_{ky}) \\ &+ \frac{\partial}{\partial z} (\gamma_{Az} \alpha_k \langle \varphi_{kz} \rangle_{kz}) \end{aligned} \quad (17)$$

where  $\alpha_k = V_k/V_m$ ,  $V_k$  being the instantaneous volume of phase  $k$  contained in the volume  $V$  and  $V_m$  is the fluid mixture volume contained in the volume  $V$ . The three quantities  $\gamma_{Ax}$ ,  $\gamma_{Ay}$ , and  $\gamma_{Az}$  are the surface porosities contained in each of the planes  $yz$ ,  $xz$ , and  $xy$ , respectively, the volume  $V$  assumed by [10] being a rectangular parallelepiped. The quantities  $\gamma_{Ax}$ ,  $\gamma_{Ay}$ , and  $\gamma_{Az}$  being directional porosities, the quantities  $\langle \varphi_{kx} \rangle_{kx}$ ,  $\langle \varphi_{ky} \rangle_{ky}$ , and  $\langle \varphi_{kz} \rangle_{kz}$  represent the phase-averaged vector components through the surfaces normal to  $x$ ,  $y$ , and  $z$  occupied by phase  $k$ . The demonstration of the relation (17) assumes that the size of the REV is not arbitrary: it should be large in comparison to the pores, size and small in comparison to the global scale of the flow [11]. According to [11], if conditions of both stability and regularity are satisfied, then the volume-averaged and surface-averaged values coincide at every point, hence there is no need to make the distinction between the surface porosities  $\gamma_{Ax}$ ,  $\gamma_{Ay}$ , and  $\gamma_{Az}$  and the volumetric one given by  $\varepsilon$ . Similarly, there is no need to make the distinction between  $\langle \varphi_{kx} \rangle_{kx}$  and  $\langle \varphi_{kx} \rangle_k$  which is the phase-average of the vector component  $\varphi_{kx}$ . According to these assertions, the relation (17) simplifies to:

$$\nabla \cdot \langle \underline{\varphi}_k \rangle = \nabla \cdot (\varepsilon \alpha_k \langle \underline{\varphi}_k \rangle_k) \quad (18)$$

which is simply a consequence of the chosen notations:  $\langle \underline{\varphi}_k \rangle \stackrel{\text{def}}{=} \varepsilon \alpha_k \langle \underline{\varphi}_k \rangle_k$  (see later in the article). The proof of what we just said is also given by [12].

## 3 Two-phase flow equations in porous media

### 3.1 Definitions and mathematical tools

We consider a two-phase flow in a porous medium. In this porous medium, we isolate a REV containing the three phases: gas, liquid, and solid (Fig. 1). This REV, denoted by  $V$ , will be the control volume for averaging. It must be large enough in comparison to the size of the pores and links between them, and small enough in comparison to the global scales of the flow. This double condition on the size of the REV is necessary for the averaged quantities to be stable and regular [11]. It should be remarked that it is not always possible in particular applications, and this condition must be kept in mind when applying the average model to a particular situation, like PEMFC modelling. The porous media in PEMFC (gas diffusion layers, microporous layers, and catalytic layers) contain two fluid phases (water and gas) and several chemical components (oxygen, hydrogen, nitrogen, and water vapour at least), so we develop a multi-constituent two-phase model for porous media. Indexing by  $k$  the general phase, by  $s$  the solid phase, and by  $m$  the liquid-gas mixture in the pores, the porosity is defined by the following relation:

$$\varepsilon \stackrel{\text{def}}{=} \frac{\sum_{k \neq s} V_k}{V} = \frac{V_m}{V} \quad (19)$$

where  $V_k$  denotes the instantaneous volume occupied by phase  $k$  (inside the REV) and  $V_m$  denotes the fluid volume

in the REV, which does not depend on time since the REV is assumed to be fixed and the porous medium is assumed to be undeformable. The phase  $k$  volume fraction, sometimes called the saturation in the porous literature, is defined by the following relation:

$$\alpha_k = \frac{V_k}{\sum_{k \neq s} V_k} = \frac{V_k}{\varepsilon V}. \quad (20)$$

From equation (20), we can deduce:

$$\sum_{k \neq s} \alpha_k = 1. \quad (21)$$

Let us define the Phase Indicator Function (PIF) by the following relation:

$$X_k(\underline{x}, t) \stackrel{\text{def}}{=} \begin{cases} 1 & \text{if the point } \underline{x} \text{ pertains to phase } k \text{ at time } t \\ 0 & \text{otherwise} \end{cases}. \quad (22)$$

It can be shown by means of the generalized function theory (*e.g.* [1, 9]):

$$\nabla X_k = -\underline{n}_k \delta_I \quad (23)$$

where  $\underline{n}_k$  is the unit vector normal to the interfaces with the other phases and pointing outwardly from phase  $k$ . The quantity  $\delta_I$  is a Dirac delta function having different interfaces as its support.  $\delta_I$  is also called the local instantaneous interfacial area concentration by [13].

The volume average of an arbitrary quantity  $\psi$  is defined by the following relation:

$$\langle \psi \rangle \stackrel{\text{def}}{=} \frac{1}{V} \int_V \psi dv. \quad (24)$$

The phase-averaged of an arbitrary quantity  $\psi_k$  pertaining to phase  $k$  is defined on the phase volume:

$$\langle \psi_k \rangle_k \stackrel{\text{def}}{=} \frac{1}{V_k} \int_{V_k} \psi_k dv. \quad (25)$$

Because of the PIF definition, it is easily shown that:

$$\langle X_k \rangle \stackrel{\text{def}}{=} \frac{1}{V} \int_V X_k dv = \frac{V_k}{V} = \varepsilon \alpha_k. \quad (26)$$

The mathematical link between the volume average (24) and the phase average (25) is:

$$\langle X_k \psi_k \rangle \stackrel{\text{def}}{=} \frac{1}{V} \int_{V_k} \psi_k dv = \frac{V_k}{V} \frac{1}{V_k} \int_{V_k} \psi_k dv = \varepsilon \alpha_k \langle \psi_k \rangle_k. \quad (27)$$

Two theorems must be introduced at this stage, which allow the averaging operator to permute with the time and space derivatives. These theorems are sometimes called the limiting forms of the Leibniz and Gauss theorem [6–8]. Here we give the version of these two theorems as derived by Gray and Lee [1]. Multiplying the gradient of an arbitrary quantity by the PIF and volume averaging, we can write:

$$\langle X_k \nabla \psi_k \rangle = \nabla \langle X_k \psi_k \rangle - \langle \psi_k \nabla X_k \rangle = \nabla \langle X_k \psi_k \rangle + \langle \psi_k \underline{n}_k \delta_I \rangle \quad (28)$$

where the last term  $\langle \psi_k \underline{n}_k \delta_I \rangle$  represents the contributions of the interfaces between phase  $k$  and the other phases. For example, if phase  $k$  is the liquid phase, the Dirac distribution  $\delta_I$  peaks to the interface with the gas on one hand, and to the interface with the solid part on the other hand. The equation (28) relates the average of a gradient to the gradient of the average. Adding a dot (scalar product) in (28), the corresponding equation for the divergence can be easily obtained. Another writing for the last term in (28) is [14]:

$$\langle \psi_k \underline{n}_k \delta_I \rangle = \frac{1}{V} \int_{A_{I,k}} \psi_k \underline{n}_k da = \frac{1}{V} \int_{A_{kf}} \psi_k \underline{n}_k da + \frac{1}{V} \int_{A_{ks}} \psi_k \underline{n}_k da \quad (29)$$

where the integral on the surface area  $A_{I,k}$  has been decomposed into the sum of two integrals: one on the interface between phase  $k$  and the other fluid phase  $f$   $A_{kf}$  and another on the interface between phase  $k$  and the solid parts  $A_{ks}$ .  $A_{I,k} = A_{kf} \cup A_{ks}$  is the total interfacial area in the volume  $V$  seen by the phase  $k$ . Putting  $\psi_k = 1$  into the equation (28), we obtain a relation giving the gradient of the product between the porosity and the phase saturation:

$$\nabla(\varepsilon \alpha_k) = -\frac{1}{V} \int_{A_{I,k}} \underline{n}_k da = -\frac{1}{V} \int_{A_{kf}} \underline{n}_k da - \frac{1}{V} \int_{A_{ks}} \underline{n}_k da. \quad (30)$$

The PIF verifies the following transport equation [9]:

$$\frac{\partial X_k}{\partial t} + \underline{v}_I \cdot \nabla X_k = 0 \quad (31)$$

where  $\underline{v}_I$  is the local instantaneous interface velocity field. Using equations (23) and (31), we can write:

$$\begin{aligned} \left\langle X_k \frac{\partial \psi_k}{\partial t} \right\rangle &= \frac{\partial}{\partial t} \langle X_k \psi_k \rangle - \left\langle \psi_k \frac{\partial X_k}{\partial t} \right\rangle \\ &= \frac{\partial}{\partial t} \langle X_k \psi_k \rangle - \langle \psi_k v_I \cdot n_k \delta_I \rangle \end{aligned} \quad (32)$$

which is the second theorem giving the link between the average of a time derivative and the time derivative of the average. The equation (32) can equivalently be written as:

$$\left\langle X_k \frac{\partial \psi_k}{\partial t} \right\rangle = \frac{\partial}{\partial t} (\varepsilon \alpha_k \langle \psi_k \rangle_k) - \frac{1}{V} \int_{A_{kf}} \psi_k v_I \cdot n_k da. \quad (33)$$

Here, there is no contribution from the interface with the solid because the solid parts are assumed to be immobile. Putting  $\psi_k = 1$  into (33), the time derivative of the phase volumetric fraction is obtained:

$$\frac{\partial}{\partial t} (\varepsilon \alpha_k) = \frac{1}{V} \int_{A_{kf}} v_I \cdot n_k da. \quad (34)$$

**Table 1.** Notations for the generalised balance equations (35) and (36).

Balance equation	$\psi_k$	$\underline{J}_k$	$\phi_k$	$\phi_I$
Mass	1	0	$r_k$	0
Species mass	$Y_{ik}$	$\underline{j}_{ik}$	$r_{ik}$	$r_{is}$
Momentum	$\underline{v}_k$	$-\underline{\sigma}_k = p_k \underline{I} - \underline{\tau}_k$	$\rho_k \underline{g} + r_k v_k^r$	$\underline{F}_I$
Total energy	$e_k + \frac{v_k^2}{2}$	$\underline{q}_k - \underline{\sigma}_k \cdot \underline{v}_k$	$\rho_k \underline{g} \cdot \underline{v}_k$	$E_I$
Enthalpy	$h_k$	$\underline{q}_k$	$\frac{D_k p_k}{Dt} + \underline{\tau}_k : \nabla \underline{v}_k + r_k h_k^r$	$H_I$
Internal energy	$e_k$	$\underline{q}_k$	$-p_k \nabla \cdot \underline{v}_k + \underline{\tau}_k : \nabla \underline{v}_k + r_k h_k^r$	$\epsilon_I$
Entropy	$s_k$	$\underline{q}_k / T_k$	$\frac{\underline{\tau}_k : \nabla \underline{v}_k}{T_k} + \underline{q}_k \cdot \nabla (1/T_k) + r_k s_k^r$	$\Delta_I$

### 3.2 Local instantaneous balance equations for two-phase flows

A general balance equation for two-phase flows before the averaging operation can be written as [6–8]:

$$\frac{\partial \rho_k \psi_k}{\partial t} + \nabla \cdot (\rho_k \psi_k \underline{v}_k) = -\nabla \cdot \underline{J}_k + \phi_k \quad (35)$$

where  $\rho_k$  is the phase density,  $\underline{v}_k$  is the phase velocity,  $\psi_k$  is an arbitrary quantity per unit mass of phase  $k$ ,  $\underline{J}_k$  is a diffusional flux and  $\phi_k$  is a general source term. The equation (35) is valid inside the phase  $k$  only. The corresponding equation valid through the interfaces between two phases (sometimes called the jump condition) reads:

$$\sum_k (\dot{m}_k \psi_k - \underline{J}_K \cdot \underline{n}_K) = \phi_I \quad (36)$$

The quantity  $\dot{m}_k$  is the mass gain for phase  $k$ , per unit surface and unit time, due to phase change (vaporisation and condensation). It is defined by the following equation:

$$\dot{m}_k \stackrel{\text{def}}{=} \rho_k (\underline{v}_I - \underline{v}_k) \cdot \underline{n}_k. \quad (37)$$

The quantity  $\phi_I$  is a general source term defined on the interfaces. Table 1 gives the values of  $\psi_k$ ,  $\underline{J}_k$ ,  $\phi_k$  and  $\phi_I$  for the different balance equations of interest: mass, species mass, momentum, and the different forms of energy.

Substituting these values into the balance equations (35) and (36), we thus obtain the detailed balance equations for phase  $k$ . The mass balances read:

$$\frac{\partial \rho_k}{\partial t} + \nabla \cdot (\rho_k \underline{v}_k) = r_k \text{ and } \sum_k \dot{m}_k = 0 \quad (38)$$

where  $\rho_k$  is the density of phase  $k$  and the symbol  $\Sigma_k$  means the summation on the two phases separated by the interface (the second Eq. (38)), as all the jump conditions, is valid on an interface only). The symbol  $r_k$  is used for the source term due to chemical reactions. The species balance equations for species  $i$  in phase  $k$  read:

$$\begin{aligned} & \frac{\partial \rho_k Y_{ik}}{\partial t} + \nabla \cdot (\rho_k Y_{ik} \underline{v}_k) = \\ & -\nabla \cdot \underline{j}_{ik} + r_{ik} \text{ and } \sum_k \left( \dot{m}_k Y_{ik} - \underline{j}_{ik} \cdot \underline{n}_k \right) = r_{is} \end{aligned} \quad (39)$$

where  $Y_{ik}$  is the mass fraction of species  $i$  in phase  $k$ ,  $\underline{j}_{ik}$  is the diffusive flux and  $r_{ik}$  is a source term due to homogeneous chemical reactions. The term  $r_{is}$  is the rate at which species  $i$  is produced by heterogeneous chemical reactions.

The momentum balance equation in phase  $k$  reads:

$$\frac{\partial \rho_k \underline{v}_k}{\partial t} + \nabla \cdot (\rho_k \underline{v}_k \underline{v}_k) = -\nabla p_k + \nabla \cdot \underline{\tau}_k + \rho_k \underline{g} + r_k v_k^r. \quad (40)$$

The term  $r_k v_k^r$  was introduced by [14] and corresponds to a supply of momentum due to chemical reactions,  $p_k$  is the pressure for phase  $k$  and  $\underline{\tau}_k$  is the viscous stress tensor. The momentum jump condition reads [9, 15]:

$$\sum_k \left( \dot{m}_k \underline{v}_k + \underline{\sigma}_k \cdot \underline{n}_k \right) = \underline{F}_I \cong \nabla_s \sigma + 2H_k \sigma \underline{n}_k. \quad (41)$$

The vector  $\underline{g}$  is the gravity acceleration,  $\underline{\sigma}_k$  is the total stress tensor (grouping the pressure and the viscous ones) and  $\underline{F}_I$  is the surface tension force per unit area. In (41)  $\sigma$  is the surface tension coefficient and  $H_k \stackrel{\text{def}}{=} -(\nabla \cdot \underline{n}_k)/2$  is the local mean curvature of the interface seen by phase  $k$ . The first term  $\nabla_s \sigma$  is the surface gradient of the surface tension, which is called the Marangoni effect in the literature.

The total energy balance equation in phase  $k$  reads:

$$\begin{aligned} & \frac{\partial \rho_k \left( e_k + \frac{v_k^2}{2} \right)}{\partial t} + \nabla \cdot \left( \rho_k \left( e_k + \frac{v_k^2}{2} \right) \underline{v}_k \right) \\ & = -\nabla \cdot \left( \underline{q}_k - \underline{\sigma}_k \cdot \underline{v}_k \right) + \rho_k \underline{g} \cdot \underline{v}_k \end{aligned} \quad (42)$$

and the total energy jump condition reads:

$$\sum_k \left( \dot{m}_k \left( e_k + \frac{v_k^2}{2} \right) - \left( \underline{q}_k - \underline{\sigma}_k \cdot \underline{v}_k \right) \cdot \underline{n}_k \right) = E_I \quad (43)$$

where  $e_k$  is the internal energy per unit mass,  $\underline{q}_k$  is the heat flux density and  $E_I$  is a possible interfacial energy source. References [16, 17] give the exact expression for the interfacial source term  $E_I$ :

$$\begin{aligned} E_I = & \rho_I \frac{D_I (e_I + v_I^2/2)}{Dt} + \dot{m}_I (e_I + v_I^2/2) - \rho_I \underline{v}_I \cdot \underline{g} \\ & + \nabla_s \cdot \underline{q}_I - \nabla_s \cdot (\sigma \underline{v}_I). \end{aligned} \quad (44)$$

In this equation,  $\rho_I$  is the interface density per unit surface,  $e_I$  is the interfacial internal energy per unit mass and  $\underline{v}_I$  is the interface velocity,  $\sigma \underline{v}_{It}$  is the product of the surface tension coefficient and the tangential interfacial velocity vector. The interfacial mass source term  $\dot{m}_I$  is defined by:

$$\dot{m}_I \stackrel{\text{def}}{=} \frac{D_I \rho_I}{Dt} + \rho_I \nabla_s \cdot \underline{v}_I. \quad (45)$$

In this study, we neglect the interface properties except the surface tension and latent heat, therefore the approximate form of equation (44) is:

$$\rho_I = \underline{q}_I = 0 \rightarrow E_I \cong -\nabla_s \cdot (\sigma \underline{v}_{It}). \quad (46)$$

The advantage of the generic balance equation (35) is that we can apply the averaging operator and theorems once to it to obtain the corresponding generic averaged balance equation. After this is done, the detailed averaged balance equations will be deduced from the generic one by employing the values given in Table 1.

The enthalpy balance equation reads:

$$\frac{\partial \rho_k h_k}{\partial t} + \nabla \cdot (\rho_k h_k \underline{v}_k) = -\nabla \cdot \underline{q}_k + \frac{D_k p_k}{Dt} + \underline{\tau}_k : \nabla \underline{v}_k + r_k h_k^r \quad (47)$$

where  $h_k^r$  is a reaction enthalpy and  $\frac{D_k p_k}{Dt}$  is the material derivative of the pressure:

$$\frac{D_k p_k}{Dt} \stackrel{\text{def}}{=} \frac{\partial p_k}{\partial t} + \underline{v}_k \cdot \nabla p_k. \quad (48)$$

The term  $\underline{\tau}_k : \nabla \underline{v}_k$  is the dissipation of mechanical energy into heat due to internal friction. The interfacial enthalpy balance reads:

$$\sum_k \left( \dot{m}_k h_k - \underline{q}_k \cdot \underline{n}_k \right) = H_I. \quad (49)$$

References [16, 17] derive the following expression for the interfacial balance of enthalpy:

$$\begin{aligned} \sum_k \left( \dot{m}_k \left( h_k + \frac{v_k^2}{2} - \underline{v}_k \cdot \underline{v}_I \right) - \underline{q}_k \cdot \underline{n}_k + \underline{\tau}_k : \underline{n}_k \cdot (\underline{v}_k - \underline{v}_I) \right) \\ = -\rho_I \frac{D_I h_I}{Dt} - \frac{D_I \sigma}{Dt} - \dot{m}_I \left( h_I - \frac{v_I^2}{2} \right) - \nabla_s \cdot \underline{q}_I. \end{aligned} \quad (50)$$

The comparison of (49) and (50) allows us to find the exact expression of the term  $H_I$ . Neglecting the interfacial properties as we have done in (46) and neglecting the mechanical effects in comparison to the thermal effects in the LHS of (50), we obtain the following approximate expression for  $H_I$ :

$$H_I \cong -\frac{D_I \sigma}{Dt} = -\frac{\partial \sigma}{\partial t} - \underline{v}_I \cdot \nabla_s \sigma. \quad (51)$$

The internal energy balance equation reads:

$$\frac{\partial \rho_k e_k}{\partial t} + \nabla \cdot (\rho_k e_k \underline{v}_k) = -\nabla \cdot \underline{q}_k - p_k \nabla \cdot \underline{v}_k + \underline{\tau}_k : \nabla \underline{v}_k + r_k h_k^r \quad (52)$$

where the source term due to homogeneous chemical reactions is proportional to the reaction enthalpy  $h_k^r$  [14]. This can be easily verified by comparing (52) and (47). The interfacial balance equation (36) reads:

$$\sum_k \left( \dot{m}_k e_k - \underline{q}_k \cdot \underline{n}_k \right) = \epsilon_I. \quad (53)$$

References [16, 17] derive the following expression for the interfacial balance of internal energy:

$$\begin{aligned} \sum_k \left( \dot{m}_k \left( e_k + \frac{v_k^2}{2} - \underline{v}_k \cdot \underline{v}_I \right) - \underline{q}_k \cdot \underline{n}_k + \underline{\tau}_k : \underline{n}_k \cdot (\underline{v}_k - \underline{v}_I) \right) \\ = -\rho_I \frac{D_I e_I}{Dt} - \dot{m}_I \left( e_I - \frac{v_I^2}{2} \right) - \nabla_s \cdot \underline{q}_I + \sigma \nabla_s \cdot \underline{v}_{It}. \end{aligned} \quad (54)$$

The comparison of (53) and (54) allows to find the exact expression of the term  $\epsilon_I$ . Neglecting the interfacial properties as we have done before and neglecting the mechanical effects in comparison to the thermal effects in the LHS of (54), we obtain the following approximate expression for  $\epsilon_I$ :

$$\epsilon_I \cong \sigma \nabla_s \cdot \underline{v}_{It}. \quad (55)$$

The entropy balance equation reads:

$$\frac{\partial \rho_k s_k}{\partial t} + \nabla \cdot (\rho_k s_k \underline{v}_k) = -\nabla \cdot \left( \frac{\underline{q}_k}{T_k} \right) + \Delta_k + r_k s_k^r. \quad (56)$$

where  $\Delta_k$  is the entropy source term, which is given by:

$$\Delta_k \stackrel{\text{def}}{=} \frac{\underline{\tau}_k : \nabla \underline{v}_k}{T_k} + \underline{q}_k \cdot \nabla \left( \frac{1}{T_k} \right) \geq 0. \quad (57)$$

The fact that  $\Delta_k \geq 0$  is the expression of the second law of thermodynamics for phase  $k$ .

References [16, 17] give the following expression of the second law of thermodynamics at the interface:

$$\sum_k \left( \dot{m}_k s_k - \frac{\underline{q}_k}{T_k} \cdot \underline{n}_k \right) + \rho_I \frac{D_I s_I}{Dt} + \dot{m}_I s_I + \nabla_s \cdot \left( \frac{\underline{q}_I}{T_I} \right) \geq 0. \quad (58)$$

Equation (36) gives for the particular case of entropy (see Table 1):

$$\sum_k \left( \dot{m}_k s_k - \frac{\underline{q}_k}{T_k} \cdot \underline{n}_k \right) = \Delta_I. \quad (59)$$

Comparing these two expressions and neglecting the interfacial properties as we have done before, the interfacial entropy source is equal to zero:

$$\Delta_I \cong 0. \quad (60)$$

One important consequence of (60) is that the local temperatures are equal at the interface [7, 8]:

$$T_L = T_G = T_I. \quad (61)$$

Equation (47), (52), and (56) are equivalent to the primary total energy equation (42). The choice of the energy equation is just a question of convenience.

## 4 Two-phase volume-averaged equations

Multiplying the phase general equation (35) by  $X_k$ , taking the volume average of the resulting equation and using the theorems and definitions of the previous section, the following averaged general balance equation is easily obtained:

$$\begin{aligned} & \frac{\partial}{\partial t} (\varepsilon \alpha_k \langle \rho_k \psi_k \rangle_k) + \nabla \cdot (\varepsilon \alpha_k \langle \rho_k \psi_k \underline{v}_k \rangle_k) \\ &= \frac{1}{V} \int_{A_{Ik}} (\dot{m}_k \psi_k - \underline{J}_k \cdot \underline{n}_k) da - \nabla \cdot (\varepsilon \alpha_k \langle \underline{J}_k \rangle_k) + \varepsilon \alpha_k \langle \phi_k \rangle_k. \end{aligned} \quad (62)$$

In the same manner, the interfacial average of equation (36) gives:

$$\sum_k \frac{1}{V} \int_{A_I} (\dot{m}_k \psi_k - \underline{J}_k \cdot \underline{n}_k) da = \frac{1}{V} \int_{A_I} \phi_I da. \quad (63)$$

### 4.1 Mass balance equation

Putting  $\psi_k = 1$ ,  $\underline{J}_k = 0$ ,  $\phi_k = r_k$  in the equation (62), the following phase k mass balance equation is obtained:

$$\frac{\partial}{\partial t} (\varepsilon \alpha_k \langle \rho_k \rangle_k) + \nabla \cdot (\varepsilon \alpha_k \langle \rho_k \underline{v}_k \rangle_k) = \varepsilon \alpha_k \langle r_k \rangle_k + \frac{1}{V} \int_{A_{Ik}} \dot{m}_k da. \quad (64)$$

Now, two different notations will be introduced. First, the phase average of the product between the density and velocity will be rewritten as:

$$\langle \rho_k \underline{v}_k \rangle_k \stackrel{\text{def}}{=} \langle \rho_k \rangle_k \overline{\underline{v}_k}^k \quad (65)$$

which defines the *Favre averaged* velocity  $\overline{\underline{v}_k}^k$ . The Favre average has been introduced in the compressible flow theories in order to avoid the appearance of double correlations between density fluctuations and velocity fluctuations. The mean velocity  $\overline{\underline{v}_k}^k$  is the *center-of-mass velocity of the k phase included in the REV*. The last term in the RHS of equation (64) corresponds to the phase k volumetric production rate due to phase change, and we introduce the following special notation for it:

$$\Gamma_k \stackrel{\text{def}}{=} \frac{1}{V} \int_{A_{Ik}} \dot{m}_k da. \quad (66)$$

Multiplying the last equation (38) by  $\delta_I$  followed by volume averaging, we obtain:

$$\sum_k \Gamma_k = 0 \quad (67)$$

showing that there is no mass accumulation on the interfaces.

### 4.2 Species mass balance equation

Putting  $\psi_k = Y_{ik}$ ,  $\underline{J}_k = \underline{j}_{ik}$ ,  $\phi_k = r_{ik}$  in the equation (62), the averaged species mass balance equation is obtained:

$$\begin{aligned} & \frac{\partial}{\partial t} (\varepsilon \alpha_k \langle \rho_k Y_{ik} \rangle_k) + \nabla \cdot (\varepsilon \alpha_k \langle \rho_k Y_{ik} \underline{v}_k \rangle_k) \\ &= \frac{1}{V} \int_{A_{Ik}} (\dot{m}_k Y_{ik} - \underline{j}_{ik} \cdot \underline{n}_k) da - \nabla \cdot (\varepsilon \alpha_k \langle \underline{j}_{ik} \rangle_k) + \varepsilon \alpha_k \langle r_{ik} \rangle_k. \end{aligned} \quad (68)$$

Multiplying the second equation (39) by  $\delta_I$  followed by volume averaging, the following averaged jump condition is obtained:

$$\sum_k \left( \Gamma_k \overline{\overline{Y_{ik}^I}} - a_{Ik} \langle \underline{j}_{ik} \cdot \underline{n}_k \rangle_I \right) = \frac{1}{V} \int_{A_{Ik}} r_{is} da. \quad (69)$$

where the following averages are defined:

$$\langle \underline{j}_{ik} \cdot \underline{n}_k \delta_I \rangle \stackrel{\text{def}}{=} a_{Ik} \langle \underline{j}_{ik} \cdot \underline{n}_k \rangle_I \quad (70)$$

$$\langle \dot{m}_k Y_{ik} \delta_I \rangle = \Gamma_k \overline{\overline{Y_{ik}^I}} \quad (71)$$

where  $a_{Ik} = \langle \delta_I \rangle$  is the interfacial area concentration seen by phase k (including the wall interface),  $\langle \underline{j}_{ik} \cdot \underline{n}_k \rangle_I$  is an interfacial average of the normal diffusive flux and  $\overline{\overline{Y_{ik}^I}}$  is the interfacial average of the mass fraction weighted by phase change.

### 4.3 Momentum balance equation

Putting  $\psi_k = \underline{v}_k$ ,  $\underline{J}_k = -\underline{\sigma}_k$ ,  $\phi_k = \rho_k \underline{g} + r_k \underline{v}_k^r$  in the equation (62), the averaged momentum balance equation is obtained:

$$\begin{aligned} & \frac{\partial}{\partial t} (\varepsilon \alpha_k \langle \rho_k \underline{v}_k \rangle_k) + \nabla \cdot (\varepsilon \alpha_k \langle \rho_k \underline{v}_k \underline{v}_k \rangle_k) \\ &= \frac{1}{V} \int_{A_{Ik}} (\dot{m}_k \underline{v}_k + \underline{\sigma}_k \cdot \underline{n}_k) da + \nabla \cdot (\varepsilon \alpha_k \langle \underline{\sigma}_k \rangle_k) \\ & \quad + \varepsilon \alpha_k \langle \rho_k \rangle_k \underline{g} + \varepsilon \alpha_k \langle r_k \underline{v}_k^r \rangle_k. \end{aligned} \quad (72)$$

We will introduce a new notation for the set of momentum interfacial terms:

$$\underline{M}_k \stackrel{\text{def}}{=} \left\langle (\dot{m}_k \underline{v}_k + \underline{\sigma}_k \cdot \underline{n}_k) \delta_I \right\rangle = \frac{1}{V} \int_{A_{Ik}} (\dot{m}_k \underline{v}_k + \underline{\sigma}_k \cdot \underline{n}_k) da. \quad (73)$$

Multiplying the jump condition (41) by  $\delta_I$  and averaging, the following averaged jump condition is obtained:

$$\sum_k \underline{M}_k = \underline{M}_I \stackrel{\text{def}}{=} \langle \underline{E}_I \delta_I \rangle \quad (74)$$

where  $\underline{M}_I$  is the interfacial momentum source due to the surface tension.

### 4.4 Total energy balance equation

Putting  $\psi_k = e_k + \frac{v_k^2}{2}$ ,  $\underline{J}_k = \underline{q}_k - \underline{\sigma}_k \cdot \underline{v}_k$ ,  $\phi_k = \rho_k \underline{g} \cdot \underline{v}_k$  in the equation (62), the averaged total energy balance equation is obtained:

$$\begin{aligned} & \frac{\partial}{\partial t} \left( \varepsilon \alpha_k \left\langle \rho_k \left( e_k + \frac{v_k^2}{2} \right) \right\rangle_k \right) + \nabla \cdot \left( \varepsilon \alpha_k \left\langle \rho_k \left( e_k + \frac{v_k^2}{2} \right) \underline{v}_k \right\rangle_k \right) \\ &= \frac{1}{V} \int_{A_{Ik}} \left( \dot{m}_k \left( e_k + \frac{v_k^2}{2} \right) - \left( \underline{q}_k - \underline{\sigma}_k \cdot \underline{v}_k \right) \cdot \underline{n}_k \right) da \\ & - \nabla \cdot \left( \varepsilon \alpha_k \left\langle \underline{q}_k - \underline{\sigma}_k \cdot \underline{v}_k \right\rangle_k \right) + \varepsilon \alpha_k \left\langle \rho_k \underline{v}_k \right\rangle_k \cdot \underline{g}. \end{aligned} \quad (75)$$

Now, we can define:

$$Q_k \stackrel{\text{def}}{=} \frac{1}{V} \int_{A_{Ik}} \left( \dot{m}_k \left( e_k + \frac{v_k^2}{2} \right) - \left( \underline{q}_k - \underline{\sigma}_k \cdot \underline{v}_k \right) \cdot \underline{n}_k \right) da. \quad (76)$$

Multiplying the jump condition (43) by  $\delta_I$  and averaging the resulting equation, the averaged form of the total energy jump condition is obtained:

$$\sum_k Q_k = Q_I \stackrel{\text{def}}{=} \langle E_I \delta_I \rangle. \quad (77)$$

#### 4.5 Enthalpy balance equation

Putting  $\psi_k = h_k$ ,  $\underline{J}_k = \underline{q}_k$ ,  $\phi_k = \frac{D_k p_k}{Dt} + \underline{\tau}_k : \nabla \underline{v}_k + r_k h_k^r$  in the equation (62), the averaged enthalpy balance equation is obtained:

$$\begin{aligned} & \frac{\partial}{\partial t} \left( \varepsilon \alpha_k \langle \rho_k h_k \rangle_k \right) + \nabla \cdot \left( \varepsilon \alpha_k \langle \rho_k h_k \underline{v}_k \rangle_k \right) \\ &= \frac{1}{V} \int_{A_{Ik}} \left( \dot{m}_k h_k - \underline{q}_k \cdot \underline{n}_k \right) da - \nabla \cdot \left( \varepsilon \alpha_k \langle \underline{q}_k \rangle_k \right) \\ & + \varepsilon \alpha_k \left\langle \frac{D_k p_k}{Dt} + \underline{\tau}_k : \nabla \underline{v}_k + r_k h_k^r \right\rangle_k. \end{aligned} \quad (78)$$

And the enthalpy mean jump condition reads (Eq. (49)):

$$\sum_k \frac{1}{V} \int_{A_I} \left( \dot{m}_k h_k - \underline{q}_k \cdot \underline{n}_k \right) da = \frac{1}{V} \int_{A_I} H_I da \cong 0 \quad (79)$$

where the term involving  $H_I$  can be neglected according to [15].

#### 4.6 Internal energy balance equation

Putting  $\psi_k = e_k$ ,  $\underline{J}_k = \underline{q}_k$ ,  $\phi_k = -p_k \nabla \cdot \underline{v}_k + \underline{\tau}_k : \nabla \underline{v}_k + r_k h_k^r$  in the equation (62), the averaged internal energy balance equation is obtained:

$$\begin{aligned} & \frac{\partial}{\partial t} \left( \varepsilon \alpha_k \langle \rho_k e_k \rangle_k \right) + \nabla \cdot \left( \varepsilon \alpha_k \langle \rho_k e_k \underline{v}_k \rangle_k \right) \\ &= \frac{1}{V} \int_{A_{Ik}} \left( \dot{m}_k e_k - \underline{q}_k \cdot \underline{n}_k \right) da - \nabla \cdot \left( \varepsilon \alpha_k \langle \underline{q}_k \rangle_k \right) \\ & + \varepsilon \alpha_k \left\langle \underline{\tau}_k : \nabla \underline{v}_k - p_k \nabla \cdot \underline{v}_k + r_k e_k^r \right\rangle_k. \end{aligned} \quad (80)$$

And the averaged internal energy jump condition reads:

$$\sum_k \frac{1}{V} \int_{A_I} \left( \dot{m}_k e_k - \underline{q}_k \cdot \underline{n}_k \right) da = \frac{1}{V} \int_{A_I} \epsilon_I da \cong 0 \quad (81)$$

where the term involving  $\epsilon_I$  can be neglected according to [15].

#### 4.7 Entropy balance equation

Putting  $\psi_k = s_k$ ,  $\underline{J}_k = \underline{q}_k / T_k$ ,  $\phi_k = \frac{\underline{\tau}_k : \nabla \underline{v}_k}{T_k} + \underline{q}_k \cdot \nabla (1/T_k) + r_k s_k^r$  in the equation (62), the averaged entropy balance equation is obtained:

$$\begin{aligned} & \frac{\partial}{\partial t} \left( \varepsilon \alpha_k \langle \rho_k s_k \rangle_k \right) + \nabla \cdot \left( \varepsilon \alpha_k \langle \rho_k s_k \underline{v}_k \rangle_k \right) \\ &= \frac{1}{V} \int_{A_{Ik}} \left( \dot{m}_k s_k - \frac{\underline{q}_k}{T_k} \cdot \underline{n}_k \right) da - \nabla \cdot \left( \varepsilon \alpha_k \left\langle \frac{\underline{q}_k}{T_k} \right\rangle_k \right) \\ & + \varepsilon \alpha_k \left\langle \frac{\underline{\tau}_k : \nabla \underline{v}_k}{T_k} + \underline{q}_k \cdot \nabla (1/T_k) + r_k s_k^r \right\rangle_k. \end{aligned} \quad (82)$$

The averaged entropy jump condition is obtained from (59):

$$\sum_k \frac{1}{V} \int_{A_I} \left( \dot{m}_k s_k - \frac{\underline{q}_k}{T_k} \cdot \underline{n}_k \right) da \cong 0. \quad (83)$$

where (60) has been taken into account.

Up to now, the mass, momentum, and energy averaged balance equations have been derived in their exact form. Nevertheless, these equations cannot be used directly since they are expressed in terms of averages of products of local quantities and integral terms. Instead, we must express all these unknown terms by closure relations. This will be done in the next sections.

## 5 The two-fluid model in porous medium

### 5.1 Useful form of the mass balance equation

Denoting by  $S_k$  the source term due to chemical reactions:

$$S_k \stackrel{\text{def}}{=} \varepsilon \alpha_k \langle r_k \rangle_k \quad (84)$$

and using the definitions (65) and (66), the mass balance equation for phase  $k$  becomes:

$$\frac{\partial}{\partial t} \left( \varepsilon \alpha_k \langle \rho_k \rangle_k \right) + \nabla \cdot \left( \varepsilon \alpha_k \langle \rho_k \underline{v}_k \rangle_k \right) = S_k + \Gamma_k \quad (85)$$

where there are two source terms in the RHS: one due to chemical reactions and the other due to phase change. These two terms must be modelled by appropriate closure laws.

### 5.2 Useful form of the species mass balance equation

In what follows, we will denote the partial density of species  $i$  in phase  $k$  as:

$$\rho_{ik} \stackrel{\text{def}}{=} \rho_k Y_{ik}. \quad (86)$$

We will also assume that the diffusion flux  $\underline{j}_{ik}$  is modelled by Fick's law:

$$\underline{j}_{ik} = -D_{ik} \nabla \rho_{ik}. \quad (87)$$

Substituting these two relations as well as (70) and (71) in (68), the following equation is obtained:

$$\begin{aligned} & \frac{\partial}{\partial t} (\varepsilon \alpha_k \langle \rho_{ik} \rangle_k) + \nabla \cdot (\varepsilon \alpha_k \langle \rho_{ik} \rangle_k \underline{\underline{v}}_k^k) \\ &= \Gamma_k \overline{\overline{Y_{ik}^I}} + a_{Ik} \langle D_{ik} \nabla \rho_{ik} \cdot \underline{\underline{n}}_k \rangle_I + \nabla \cdot (\varepsilon \alpha_k \langle D_{ik} \nabla \rho_{ik} \rangle_k) + S_{ik} \end{aligned} \quad (88)$$

where the last term is due to chemical reactions:

$$S_{ik} \stackrel{\text{def}}{=} \varepsilon \alpha_k \langle r_{ik} \rangle_k. \quad (89)$$

Assuming that the diffusivity of the species  $i$  in phase  $k$  is constant at the scale of the averaging volume, the diffusive term can be rewritten as:

$$\begin{aligned} \nabla \cdot (\varepsilon \alpha_k \langle D_{ik} \nabla \rho_{ik} \rangle_k) &= \nabla \cdot (D_{ik} \langle X_k \nabla \rho_{ik} \rangle) \\ &= \nabla \cdot (D_{ik} (\nabla (\varepsilon \alpha_k \langle \rho_{ik} \rangle_k) + \langle \rho_{ik} \underline{\underline{n}}_k \delta_I \rangle)) \end{aligned} \quad (90)$$

where the theorem relating the average of a gradient to the gradient of the average has been used.

Substituting (86) and (90) into (88), the following equation is obtained:

$$\begin{aligned} & \frac{\partial}{\partial t} (\varepsilon \alpha_k \langle \rho_k Y_{ik} \rangle_k) + \nabla \cdot (\varepsilon \alpha_k \langle \rho_k Y_{ik} \underline{\underline{v}}_k \rangle_k) \\ &= \Gamma_k \overline{\overline{Y_{ik}^I}} + a_{Ik} \langle D_{ik} \nabla \rho_{ik} \cdot \underline{\underline{n}}_k \rangle_I + \nabla \cdot (D_{ik} (\nabla (\varepsilon \alpha_k \langle \rho_{ik} \rangle_k) \\ &+ \langle \rho_{ik} \underline{\underline{n}}_k \delta_I \rangle)) + S_{ik}. \end{aligned} \quad (91)$$

Following [18], the term  $\langle \rho_{ik} \underline{\underline{n}}_k \delta_I \rangle$  is neglected and the term  $a_{Ik} \langle D_{ik} \nabla \rho_{ik} \cdot \underline{\underline{n}}_k \rangle_I$  is attributed to the adsorption/desorption phenomena:

$$\Sigma_{ik} \stackrel{\text{def}}{=} a_{Ik} \langle D_{ik} \nabla \rho_{ik} \cdot \underline{\underline{n}}_k \rangle_I \quad (92)$$

The final form of the equation (91) reads:

$$\begin{aligned} & \frac{\partial}{\partial t} (\varepsilon \alpha_k \langle \rho_k \rangle_k \overline{\overline{Y_{ik}^k}}) + \nabla \cdot (\varepsilon \alpha_k \langle \rho_k \rangle_k \overline{\overline{Y_{ik} \underline{\underline{v}}_k^k}}) \\ &= \nabla \cdot (D_{ik} \nabla (\varepsilon \alpha_k \langle \rho_k \rangle_k \overline{\overline{Y_{ik}^k}})) + \Gamma_k Y_{ik}^I + \Sigma_{ik} + S_{ik}. \end{aligned} \quad (93)$$

### 5.3 Useful form of the momentum balance equation

Introducing the Favre average and the definition (73), the momentum balance equation (72) becomes:

$$\begin{aligned} & \frac{\partial}{\partial t} (\varepsilon \alpha_k \langle \rho_k \rangle_k \overline{\overline{\underline{\underline{v}}_k^k}}) + \nabla \cdot (\varepsilon \alpha_k \langle \rho_k \rangle_k \overline{\overline{\underline{\underline{v}}_k^k}}) \\ &= \frac{1}{V} \int_{A_{kf}} (\dot{m}_k \underline{\underline{v}}_k + (\underline{\underline{\tau}}_k - p_k \underline{\underline{I}}) \cdot \underline{\underline{n}}_k) da \\ &+ \frac{1}{V} \int_{A_{ks}} (\dot{m}_k \underline{\underline{v}}_k + (\underline{\underline{\tau}}_k - p_k \underline{\underline{I}}) \cdot \underline{\underline{n}}_k) da - \nabla (\varepsilon \alpha_k \langle p_k \rangle_k) \\ &+ \nabla \cdot (\varepsilon \alpha_k \langle \underline{\underline{\tau}}_k \rangle_k) + \varepsilon \alpha_k \langle \rho_k \rangle_k \underline{\underline{g}} + \varepsilon \alpha_k \langle r_k \underline{\underline{v}}_k^r \rangle_k. \end{aligned} \quad (94)$$

In this equation, the total stress tensor has been decomposed into a pressure term and a viscous stress tensor (Table 1). The interfacial term has been split into two integrals: the first integral concerns the gas-liquid interface  $A_{kf}$  and the second one concerns the wall surface  $A_{ks}$ . In the LHS of (94), we have the Favre average of the tensorial product of the velocity by itself  $\overline{\overline{\underline{\underline{v}}_k^k}}$ . In order to make the dispersion tensor appear, the local velocity is decomposed into its mean value and a fluctuating component:

$$\underline{\underline{v}}_k \stackrel{\text{def}}{=} \overline{\overline{\underline{\underline{v}}_k^k}} + \underline{\underline{v}}_k'. \quad (95)$$

The Favre average of the equation (95) shows that  $\overline{\overline{\underline{\underline{v}}_k^k}} = 0$ , *i.e.*, the average of a fluctuation is zero, and we deduce immediately that the average of a product is equal to the product of the averages, in addition to the average of the product of fluctuations:

$$\overline{\overline{\underline{\underline{v}}_k^k}} = \overline{\overline{\underline{\underline{v}}_k^k}} \overline{\overline{\underline{\underline{v}}_k^k}} + \overline{\overline{\underline{\underline{v}}_k' \underline{\underline{v}}_k'^k}}. \quad (96)$$

Substituting (96) into (94) and introducing the following notation for the dispersion tensor:

$$\underline{\underline{\tau}}_k^T \stackrel{\text{def}}{=} - \langle \rho_k \rangle_k \overline{\overline{\underline{\underline{v}}_k' \underline{\underline{v}}_k'^k}}. \quad (97)$$

The tensor  $\underline{\underline{\tau}}_k^T$  is called the Reynolds stress tensor in the turbulence community when a time or ensemble average is used. Here, we prefer to call it the dispersion tensor since a spatial average is used. Substituting (96) and (97) into (94), the momentum equation becomes:

$$\begin{aligned} & \frac{\partial}{\partial t} (\varepsilon \alpha_k \langle \rho_k \rangle_k \overline{\overline{\underline{\underline{v}}_k^k}}) + \nabla \cdot (\varepsilon \alpha_k \langle \rho_k \rangle_k \overline{\overline{\underline{\underline{v}}_k^k}}) \\ &= \frac{1}{V} \int_{A_{Ik}} (\dot{m}_k \underline{\underline{v}}_k + (\underline{\underline{\tau}}_k - p_k \underline{\underline{I}}) \cdot \underline{\underline{n}}_k) da \\ &+ \frac{1}{V} \int_{A_{wk}} (\dot{m}_k \underline{\underline{v}}_k + (\underline{\underline{\tau}}_k - p_k \underline{\underline{I}}) \cdot \underline{\underline{n}}_k) da - \nabla (\varepsilon \alpha_k \langle p_k \rangle_k) \\ &+ \nabla \cdot (\varepsilon \alpha_k (\langle \underline{\underline{\tau}}_k \rangle_k + \underline{\underline{\tau}}_k^T)) + \varepsilon \alpha_k \langle \rho_k \rangle_k \underline{\underline{g}} + \varepsilon \alpha_k \langle r_k \underline{\underline{v}}_k^r \rangle_k. \end{aligned} \quad (98)$$

Following [19], we can use the momentum jump condition (74) in order to introduce the surface tension, for example, in the liquid phase:

$$\begin{aligned} & \frac{1}{V} \int_{A_{Ik}} (\dot{m}_L \underline{\underline{v}}_L + (\underline{\underline{\tau}}_L - p_L \underline{\underline{I}}) \cdot \underline{\underline{n}}_L) da \\ &= - \frac{1}{V} \int_{A_{Ik}} (\dot{m}_G \underline{\underline{v}}_G + (\underline{\underline{\tau}}_G - p_G \underline{\underline{I}}) \cdot \underline{\underline{n}}_G - \nabla_s \sigma + 2H_L \sigma \underline{\underline{n}}_L) da. \end{aligned} \quad (99)$$

The first term, due to phase change, is sometimes called the recoil force, and we can use the interfacial average weighted by phase change as in (71) to express it:

$$\frac{1}{V} \int_{A_{Ik}} \dot{m}_k \underline{\underline{v}}_k da = \Gamma_k \overline{\overline{\underline{\underline{v}}_k^I}} \stackrel{\text{def}}{=} \Gamma_k \underline{\underline{V}}_\Gamma. \quad (100)$$

In the last definition, it is not useful to put a  $k$  index on the mean velocity weighted by phase change  $\underline{\underline{V}}_\Gamma$  since this

mean velocity should not depend on the phase considered [20, 21].

Substituting (99) into (98) written for the liquid phase:

$$\begin{aligned} & \frac{\partial}{\partial t} \left( \varepsilon \alpha_L \langle \rho_L \rangle_L \bar{\underline{v}}_L^L \right) + \nabla \cdot \left( \varepsilon \alpha_L \langle \rho_L \rangle_L \bar{\underline{v}}_L^L \bar{\underline{v}}_L^L \right) \\ &= -\frac{1}{V} \int_{A_I} \left( \dot{m}_G \underline{v}_G - \left( \underline{\tau}_G - p_G \underline{I} \right) \cdot \underline{n}_L - \nabla_s \sigma + 2H_L \sigma \underline{n}_L \right) da \\ & \quad + \frac{1}{V} \int_{A_{wL}} \left( \dot{m}_L \underline{v}_L + \left( \underline{\tau}_L - p_L \underline{I} \right) \cdot \underline{n}_L \right) da - \nabla \left( \varepsilon \alpha_L \langle p_L \rangle_L \right) \\ & \quad + \nabla \cdot \left( \varepsilon \alpha_L \left( \left\langle \underline{\tau}_L \right\rangle_L + \underline{\tau}_L^T \right) \right) + \varepsilon \alpha_L \langle \rho_L \rangle_L \underline{g} + \varepsilon \alpha_L \langle r_L \underline{v}_L^r \rangle_L \end{aligned} \quad (101)$$

Decomposing  $p_L$  and  $p_G$  into their mean and fluctuating components, the previous equation becomes:

See the Equation (102) bottom of the page

$A_{I,k}$  being decomposed into the interfacial area  $A_I$  and the wall area in contact to the liquid  $A_{wL}$ , the first and third terms in the RHS of (102) can be transformed into:

$$\begin{aligned} & -\frac{\langle p_G \rangle_G}{V} \int_{A_I} \underline{n}_L da - \frac{\langle p_L \rangle_L}{V} \int_{A_{wL}} \underline{n}_L da \\ &= \langle p_G \rangle_G \nabla \left( \varepsilon \alpha_L \right) + \left( \langle p_G \rangle_G - \langle p_L \rangle_L \right) \frac{1}{V} \int_{A_{wL}} \underline{n}_L da. \end{aligned} \quad (103)$$

Assuming that the mean curvature  $H_L$  and the surface tension  $\sigma$  do not fluctuate, the surface tension terms in (102) can be rewritten as:

$$\begin{aligned} & -\frac{1}{V} \int_{A_I} \left( 2H_L \sigma \underline{n}_L - \nabla_s \sigma \right) da \\ &= 2H_L \sigma \left( \nabla \left( \varepsilon \alpha_L \right) + \frac{1}{V} \int_{A_{wL}} \underline{n}_L da \right) + \frac{1}{V} \int_{A_I} \nabla_s \sigma da. \end{aligned} \quad (104)$$

Grouping the mean pressure terms and the surface tension terms appearing in (102), we obtain:

$$\begin{aligned} & \frac{\partial}{\partial t} \left( \varepsilon \alpha_L \langle \rho_L \rangle_L \bar{\underline{v}}_L^L \right) + \nabla \cdot \left( \varepsilon \alpha_L \langle \rho_L \rangle_L \bar{\underline{v}}_L^L \bar{\underline{v}}_L^L \right) = -\frac{\langle p_G \rangle_G}{V} \int_{A_I} \underline{n}_L da - \frac{1}{V} \int_{A_I} \left( \dot{m}_G \underline{v}_G - \left( \underline{\tau}_G - p'_G \underline{I} \right) \cdot \underline{n}_L - \nabla_s \sigma + 2H_L \sigma \underline{n}_L \right) da \\ & \quad - \frac{\langle p_L \rangle_L}{V} \int_{A_{wL}} \underline{n}_L da + \frac{1}{V} \int_{A_{wL}} \left( \dot{m}_L \underline{v}_L + \left( \underline{\tau}_L - p'_L \underline{I} \right) \cdot \underline{n}_L \right) da - \nabla \left( \varepsilon \alpha_L \langle p_L \rangle_L \right) + \nabla \cdot \left( \varepsilon \alpha_L \left( \left\langle \underline{\tau}_L \right\rangle_L + \underline{\tau}_L^T \right) \right) \\ & \quad + \varepsilon \alpha_L \langle \rho_L \rangle_L \underline{g} + \varepsilon \alpha_L \langle r_L \underline{v}_L^r \rangle_L. \end{aligned} \quad (102)$$

$$\begin{aligned} & \frac{\partial}{\partial t} \left( \varepsilon \alpha_L \langle \rho_L \rangle_L \bar{\underline{v}}_L^L \right) + \nabla \cdot \left( \varepsilon \alpha_L \langle \rho_L \rangle_L \bar{\underline{v}}_L^L \bar{\underline{v}}_L^L \right) = \Gamma_{LI} \underline{V}_{\Gamma I} + \Gamma_{Lw} \underline{V}_{\Gamma w} - \varepsilon \alpha_L \nabla \langle p_L \rangle_L \\ & \quad + \left( \langle p_G \rangle_G - \langle p_L \rangle_L + 2H_L \sigma \right) \left( \nabla \left( \varepsilon \alpha_L \right) + \frac{1}{V} \int_{A_{wL}} \underline{n}_L da \right) + \frac{1}{V} \int_{A_I} \nabla_s \sigma da + \frac{1}{V} \int_{A_I} \left( \underline{\tau}_G - p'_G \underline{I} \right) \cdot \underline{n}_L da \\ & \quad + \frac{1}{V} \int_{A_{wL}} \left( \underline{\tau}_L - p'_L \underline{I} \right) \cdot \underline{n}_L da + \nabla \cdot \left( \varepsilon \alpha_L \left( \left\langle \underline{\tau}_L \right\rangle_L + \underline{\tau}_L^T \right) \right) + \varepsilon \alpha_L \langle \rho_L \rangle_L \underline{g} + \varepsilon \alpha_L \langle r_L \underline{v}_L^r \rangle_L. \end{aligned} \quad (106)$$

$$\begin{aligned} & -\nabla \left( \varepsilon \alpha_L \langle p_L \rangle_L \right) - \frac{\langle p_G \rangle_G}{V} \int_{A_I} \underline{n}_L da - \frac{\langle p_L \rangle_L}{V} \int_{A_{wL}} \underline{n}_L da \\ & - \frac{1}{V} \int_{A_I} \left( 2H_L \sigma \underline{n}_L - \nabla_s \sigma \right) da = -\varepsilon \alpha_L \nabla \langle p_L \rangle_L + \left( \langle p_G \rangle_G - \langle p_L \rangle_L \right) \\ & \quad + 2H_L \sigma \left( \nabla \left( \varepsilon \alpha_L \right) + \frac{1}{V} \int_{A_{wL}} \underline{n}_L da \right) + \frac{1}{V} \int_{A_I} \nabla_s \sigma da. \end{aligned} \quad (105)$$

The recoil force is modelled by (100) [20, 21]. Grouping all these results, the momentum equation for the liquid phase (102) becomes:

See the Equation (106) bottom of the page

For the gas phase, we will conserve the primitive form without using the momentum jump condition. As a consequence, the equation (98) becomes for the gas phase:

$$\begin{aligned} & \frac{\partial}{\partial t} \left( \varepsilon \alpha_G \langle \rho_G \rangle_G \bar{\underline{v}}_G^G \right) + \nabla \cdot \left( \varepsilon \alpha_G \langle \rho_G \rangle_G \bar{\underline{v}}_G^G \bar{\underline{v}}_G^G \right) \\ &= -\Gamma_{LI} \underline{V}_{\Gamma I} - \Gamma_{Lw} \underline{V}_{\Gamma w} - \varepsilon \alpha_G \nabla \langle p_G \rangle_G \\ & \quad + \frac{1}{V} \int_{A_I} \left( \underline{\tau}_G - p'_G \underline{I} \right) \cdot \underline{n}_G da + \frac{1}{V} \int_{A_{wG}} \left( \underline{\tau}_G - p'_G \underline{I} \right) \cdot \underline{n}_G da \\ & \quad + \nabla \cdot \left( \varepsilon \alpha_G \left( \left\langle \underline{\tau}_G \right\rangle_G + \underline{\tau}_G^T \right) \right) + \varepsilon \alpha_G \langle \rho_G \rangle_G \underline{g} + \varepsilon \alpha_G \langle r_G \underline{v}_G^r \rangle_G \end{aligned} \quad (107)$$

#### 5.4 Useful forms of the energy equation

Here we follow the development of [14] and choose the enthalpy balance equation (78) as the departure point. First of all, the dissipative term is assumed to be negligible:

$$\left\langle \underline{\tau}_k : \nabla \underline{v}_k \right\rangle_k \cong 0. \quad (108)$$

This term is really important for very viscous fluids, such as liquid polymers. Here we deal with water and air, which are weakly viscous; therefore the assumption (108) is not too strong. Now we must examine the average of the pressure material derivative:

$$\frac{D_k p_k}{Dt} = \frac{\partial p_k}{\partial t} + \underline{v}_k \cdot \nabla p_k. \quad (109)$$

For the time derivative, the relations (29) and (32) can be used:

$$\begin{aligned} \varepsilon \alpha_k \left\langle \frac{\partial p_k}{\partial t} \right\rangle_k &= \left\langle X_k \frac{\partial p_k}{\partial t} \right\rangle = \frac{\partial}{\partial t} (\varepsilon \alpha_k \langle p_k \rangle_k) \\ &\quad - \frac{1}{V} \int_{A_{kf}} p_k \underline{v}_I \cdot \underline{n}_k da - \frac{1}{V} \int_{A_{ks}} p_k \underline{v}_I \cdot \underline{n}_k da. \end{aligned} \quad (110)$$

The term  $\underline{v}_k \cdot \nabla p_k$  in (109) is more complicated since it is non-linear. Faust and Mercer [14] assume that the phase velocity and the pressure gradient are weakly correlated to obtain the following approximation:

$$\begin{aligned} \langle X_k \underline{v}_k \cdot \nabla p_k \rangle &\cong \overline{\underline{v}_k}^k \cdot \langle X_k \nabla p_k \rangle \\ &= \overline{\underline{v}_k}^k \cdot [\nabla \langle X_k p_k \rangle + \langle p_k \underline{n}_k \delta_I \rangle] \\ &= \overline{\underline{v}_k}^k \cdot \left[ \nabla (\varepsilon \alpha_k \langle p_k \rangle_k) + \frac{1}{V} \int_{A_{kf}} p_k \underline{n}_k da + \frac{1}{V} \int_{A_{ks}} p_k \underline{n}_k da \right] \end{aligned} \quad (111)$$

where (28) and (29) have been used. Decomposing the pressure into phase-average and fluctuating parts:

$$p_k = \langle p_k \rangle_k + p'_k \quad (112)$$

then the equation (111) can be rewritten into the following equivalent form:

$$\langle X_k \underline{v}_k \cdot \nabla p_k \rangle \cong \overline{\underline{v}_k}^k \cdot \left[ \varepsilon \alpha_k \nabla \langle p_k \rangle_k + \frac{1}{V} \int_{A_{kf}} p'_k \underline{n}_k da + \frac{1}{V} \int_{A_{ks}} p'_k \underline{n}_k da \right] \quad (113)$$

by using the relation (30). Substituting (108), (109), and (113) into (78) gives:

$$\begin{aligned} &\frac{\partial}{\partial t} (\varepsilon \alpha_k \langle \rho_k h_k \rangle_k) + \nabla \cdot (\varepsilon \alpha_k \langle \rho_k h_k \underline{v}_k \rangle_k) \\ &= \frac{1}{V} \int_{A_{kf}} (\dot{m}_k h_k - \underline{q}_k \cdot \underline{n}_k) da + \frac{1}{V} \int_{A_{ks}} (\dot{m}_k h_k - \underline{q}_k \cdot \underline{n}_k) da \\ &\quad - \nabla \cdot (\varepsilon \alpha_k \langle \underline{q}_k \rangle_k) + \varepsilon \alpha_k \langle r_k h_k^r \rangle_k + \frac{\partial}{\partial t} (\varepsilon \alpha_k \langle p_k \rangle_k) \\ &\quad - \frac{1}{V} \int_{A_{kf}} p_k \underline{v}_I \cdot \underline{n}_k da - \frac{1}{V} \int_{A_{ks}} p_k \underline{v}_I \cdot \underline{n}_k da \\ &\quad + \overline{\underline{v}_k}^k \cdot \left[ \varepsilon \alpha_k \nabla \langle p_k \rangle_k + \frac{1}{V} \int_{A_{kf}} p'_k \underline{n}_k da + \frac{1}{V} \int_{A_{ks}} p'_k \underline{n}_k da \right]. \end{aligned} \quad (114)$$

It is assumed that there is no phase change between a fluid phase and the solid phase, hence the phase change term

$\dot{m}_k h_k$  gives no contribution on the solid surface  $A_{ks}$ . Let us introduce some new notations for the integral terms:

$$\Gamma_k h_k^\Gamma \stackrel{\text{def}}{=} \frac{1}{V} \int_{A_{kf}} \dot{m}_k h_k da + \frac{1}{V} \int_{A_{ks}} \dot{m}_k h_k da = \frac{1}{V} \int_{A_{kf}} \dot{m}_k h_k da. \quad (115)$$

$$q_{kf} \stackrel{\text{def}}{=} -\frac{1}{V} \int_{A_{kf}} \underline{q}_k \cdot \underline{n}_k da \quad q_{ks} \stackrel{\text{def}}{=} -\frac{1}{V} \int_{A_{ks}} \underline{q}_k \cdot \underline{n}_k da \quad (116)$$

$$q''_{kf} \stackrel{\text{def}}{=} \overline{\underline{v}_k}^k \cdot \frac{1}{V} \int_{A_{kf}} p'_k \underline{n}_k da \quad q''_{ks} \stackrel{\text{def}}{=} \overline{\underline{v}_k}^k \cdot \frac{1}{V} \int_{A_{ks}} p'_k \underline{n}_k da. \quad (117)$$

Strangely, the two terms  $-\frac{1}{V} \int_{A_{kf}} p_k \underline{v}_I \cdot \underline{n}_k da$  and  $-\frac{1}{V} \int_{A_{ks}} p_k \underline{v}_I \cdot \underline{n}_k da$  are included in the term  $\Gamma_k h_k^\Gamma$  by [14]. Making the same choice, equation (114) begins:

$$\begin{aligned} &\frac{\partial}{\partial t} (\varepsilon \alpha_k \langle \rho_k h_k \rangle_k) + \nabla \cdot (\varepsilon \alpha_k \langle \rho_k h_k \underline{v}_k \rangle_k) = \Gamma_k h_k^\Gamma + q_{kf} + q_{ks} \\ &\quad - \nabla \cdot (\varepsilon \alpha_k \langle \underline{q}_k \rangle_k) + \varepsilon \alpha_k \langle r_k h_k^r \rangle_k + \frac{\partial}{\partial t} (\varepsilon \alpha_k \langle p_k \rangle_k) \\ &\quad + \varepsilon \alpha_k \overline{\underline{v}_k}^k \cdot \nabla \langle p_k \rangle_k + q''_{kf} + q''_{ks}. \end{aligned} \quad (118)$$

The term  $\Gamma_k h_k^\Gamma$  represents the interfacial transfer of enthalpy associated to the transfer of mass by evaporation or condensation. The terms  $q_{kf}$  and  $q_{ks}$  represent the interfacial conduction terms between the two fluid phases on one hand and between phase  $k$  and the solid phase on the other hand. The term  $\langle r_k h_k^r \rangle_k$  represents the reaction enthalpy due to chemical reactions. The last two terms  $q''_{kf}$  and  $q''_{ks}$  are the mechanical powers of the interfacial fluctuating pressure forces in the mean velocity. Introducing a Favre average value for the enthalpy, we can write:

$$\langle \rho_k h_k \rangle_k = \langle \rho_k \rangle_k \overline{\overline{h_k}}^k \quad (119)$$

$$\langle \rho_k h_k \underline{v}_k \rangle_k = \langle \rho_k \rangle_k \overline{\overline{h_k \underline{v}_k}}^k = \langle \rho_k \rangle_k \left( \overline{\overline{h_k}}^k \overline{\overline{\underline{v}_k}}^k + \overline{\overline{h'_k \underline{v}'_k}}^k \right) \quad (120)$$

where  $\overline{\overline{h'_k \underline{v}'_k}}^k$  is a correlation between the fluctuating enthalpy and velocity, we call it the dispersion vector and denote it as follows:

$$\underline{q}_k^d \stackrel{\text{def}}{=} \langle \rho_k \rangle_k \overline{\overline{h'_k \underline{v}'_k}}^k. \quad (121)$$

Substituting (119) and (121) into (118) gives:

$$\begin{aligned} &\frac{\partial}{\partial t} (\varepsilon \alpha_k \langle \rho_k \rangle_k \overline{\overline{h_k}}^k) + \nabla \cdot (\varepsilon \alpha_k \langle \rho_k \rangle_k \overline{\overline{h_k}}^k \overline{\overline{\underline{v}_k}}^k) = \Gamma_k h_k^\Gamma + q_{kf} + q_{ks} \\ &\quad - \nabla \cdot (\varepsilon \alpha_k (\langle \underline{q}_k \rangle_k + \underline{q}_k^d)) + \varepsilon \alpha_k \langle r_k h_k^r \rangle_k + \frac{\partial}{\partial t} (\varepsilon \alpha_k \langle p_k \rangle_k) \\ &\quad + \varepsilon \alpha_k \overline{\underline{v}_k}^k \cdot \nabla \langle p_k \rangle_k + q''_{kf} + q''_{ks}. \end{aligned} \quad (122)$$

The modeling of the average molecular heat flux  $\langle \underline{q}_k \rangle_k$  uses the Fourier's law:

$$\underline{q}_k = -k_k \nabla T_k. \quad (123)$$

Assuming that the conductivity  $k_k$  does not vary significantly at the scale of the REV:

$$\begin{aligned} \varepsilon \alpha_k \langle \underline{q}_k \rangle_k &= -k_k \langle X_k \nabla T_k \rangle_k \\ &= -k_k \left( \nabla (\varepsilon \alpha_k \langle T_k \rangle_k) + \frac{1}{V} \int_{A_{kf}} T_k \underline{n}_k da + \frac{1}{V} \int_{A_{ks}} T_k \underline{n}_k da \right). \end{aligned} \quad (124)$$

As done previously for the pressure, we decompose the temperature  $T_k$  into its phase average plus a fluctuation:

$$T_k \stackrel{\text{def}}{=} \langle T_k \rangle_k + T'_k. \quad (125)$$

Introducing (125) into (124) and using (30), we obtain:

$$\begin{aligned} \varepsilon \alpha_k \langle \underline{q}_k \rangle_k &= -k_k \left( \varepsilon \alpha_k \nabla \langle T_k \rangle_k + \frac{1}{V} \int_{A_{kf}} T'_k \underline{n}_k da + \frac{1}{V} \int_{A_{ks}} T'_k \underline{n}_k da \right) \end{aligned} \quad (126)$$

where the two surface integrals represent the decreased conduction rate due to the tortuosity of the medium, we define the tortuosity vector for the heat flux as:

$$\underline{\vartheta}_k \stackrel{\text{def}}{=} \frac{1}{V} \int_{A_{kf}} T'_k \underline{n}_k da + \frac{1}{V} \int_{A_{ks}} T'_k \underline{n}_k da. \quad (127)$$

Hence, equation (126) becomes:

$$\varepsilon \alpha_k \langle \underline{q}_k \rangle_k = -k_k (\varepsilon \alpha_k \nabla \langle T_k \rangle_k + \underline{\vartheta}_k). \quad (128)$$

Assuming that the dispersion vector can be modelled similarly by a diffusion effect, we introduce the dispersion tensor such that:

$$\varepsilon \alpha_k \underline{q}_k^d = -\underline{k}_k^d \cdot (\varepsilon \alpha_k \nabla \langle T_k \rangle_k + \underline{\vartheta}_k). \quad (129)$$

Substituting (128) and (129) into equation (122), this equation becomes:

$$\begin{aligned} &\frac{\partial}{\partial t} (\varepsilon \alpha_k \langle \rho_k \rangle_k \overline{\overline{h_k}}) + \nabla \cdot (\varepsilon \alpha_k \langle \rho_k \rangle_k \overline{\overline{h_k}} \underline{\underline{v_k}}) \\ &= \Gamma_k h_k^\Gamma + q_{kf} + q_{ks} + \nabla \cdot \left( (k_k \underline{\underline{I}} + \underline{\underline{k}}_k^d) \cdot (\varepsilon \alpha_k \nabla \langle T_k \rangle_k + \underline{\vartheta}_k) \right) \\ &+ \varepsilon \alpha_k \langle r_k h_k^r \rangle_k + \frac{\partial}{\partial t} (\varepsilon \alpha_k \langle p_k \rangle_k) + \varepsilon \alpha_k \underline{\underline{v}}_k^k \cdot \nabla \langle p_k \rangle_k + q''_{kf} + q''_{ks}. \end{aligned} \quad (130)$$

For the solid phase, the equation is simpler since there is no velocity (hence no dispersion), no phase change, no chemical reaction... in it, hence we can write the enthalpy equation for the solid phase as:

$$\frac{\partial}{\partial t} \left( (1 - \varepsilon) \langle \rho_s \rangle_s \overline{\overline{h_s}} \right) = q_{st} + q_{sg} + \nabla \cdot (k_s ((1 - \varepsilon) \nabla \langle T_s \rangle_s + \underline{\vartheta}_s)). \quad (131)$$

where  $q_{st}$  and  $q_{sg}$  denote the heat exchanges between the solid and the liquid on one hand and between the solid and the gas on the other hand.

## 6 Simplifications currently adopted in the case of PEMFC

### 6.1 Simplification of the momentum balance equations

Faust and Mercer [14] made the following simplification of the momentum balance equation for phase  $k$ . Starting from our equation (72) and neglecting the inertial terms (including the phase change term and the chemical one, which is justifiable in porous media since viscous and pressure effects are predominant), the remaining equation is:

$$0 \cong \frac{1}{V} \int_{A_{jk}} \underline{\underline{\sigma}}_k \cdot \underline{n}_k da - \varepsilon \alpha_k \nabla \langle p_k \rangle_k + \nabla \cdot (\varepsilon \alpha_k \langle \underline{\underline{\tau}}_k \rangle_k) + \varepsilon \alpha_k \langle \rho_k \rangle_k \underline{g}. \quad (132)$$

Then [14] introduces the following modeling of the interfacial term plus the phase viscous diffusion:

$$\frac{1}{V} \int_{A_{jk}} \underline{\underline{\sigma}}_k \cdot \underline{n}_k da + \nabla \cdot (\varepsilon \alpha_k \langle \underline{\underline{\tau}}_k \rangle_k) = \underline{\underline{K}}^{-1} \cdot \frac{\varepsilon \alpha_k \mu_k}{K_{rk}} (\langle \underline{v}_s \rangle - \langle \underline{v}_k \rangle). \quad (133)$$

where  $\underline{\underline{K}}$  is the local intrinsic permeability tensor,  $K_{rk}$  is the dimensionless relative permeability for phase  $k$  and  $\mu_k$  is phase  $k$ 's viscosity. Substituting (133) into (132), we obtain:

$$\nabla \langle p_k \rangle_k - \langle \rho_k \rangle_k \underline{g} = \underline{\underline{K}}^{-1} \cdot \frac{\mu_k}{K_{rk}} (\langle \underline{v}_s \rangle - \langle \underline{v}_k \rangle). \quad (134)$$

Here we assume that the solid phase is immobile ( $\langle \underline{v}_s \rangle = 0$ ) and  $\langle \underline{v}_k \rangle$  is the filtration velocity, which is defined by [14] as:

$$\langle \underline{v}_k \rangle = \varepsilon \alpha_k \langle \underline{v}_k \rangle_k. \quad (135)$$

Hence, we obtain:

$$\langle \underline{v}_k \rangle_k = \frac{K_{rk}}{\varepsilon \alpha_k \mu_k} (\nabla \langle p_k \rangle_k - \langle \rho_k \rangle_k \underline{g}). \quad (136)$$

We have retrieved the result (5) given by [4]. The closure relation (136) is used as an approximation for  $\overline{\overline{v_k}}^k$  by [22] in the case of PEMFC.

For the flows in the channels of the bipolar plates, [23] adopted the simplest forms of our equations (106) and (107). Assuming that the flows in the channels remain laminar, they retain the following two-fluid model equations:

$$\begin{aligned} &\frac{\partial}{\partial t} (\alpha_L \langle \rho_L \rangle_L \overline{\overline{v_L}}^L) + \nabla \cdot (\alpha_L \langle \rho_L \rangle_L \overline{\overline{v_L}}^L \underline{\underline{v_L}}^L) \\ &= -\alpha_L \nabla P + \underline{F}_s - \underline{R}_{LG} + \nabla \cdot (\alpha_L \langle \underline{\underline{\tau}}_L \rangle_L) + \alpha_L \langle \rho_L \rangle_L \underline{g} \end{aligned} \quad (137)$$

$$\begin{aligned} & \frac{\partial}{\partial t} (\alpha_G \langle \rho_G \rangle_G \overline{\underline{v}}_G^G) + \nabla \cdot (\alpha_G \langle \rho_G \rangle_G \overline{\underline{v}}_G^G \overline{\underline{v}}_G^G) \\ &= -\alpha_G \nabla P + \underline{F}_s + \underline{R}_{LG} + \nabla \cdot (\alpha_G \langle \underline{\tau}_G \rangle_G) + \alpha_G \langle \rho_G \rangle_G \underline{g} \end{aligned} \quad (138)$$

where the indices  $L$  and  $G$  denote the liquid and gas phases,  $\underline{R}_{LG}$  is the volumetric friction between phases and  $\underline{F}_s$  is a surface tension source term.

## 6.2 Simplification of the species mass balance equation

Tardy [22] starts from the equation (93) and neglects the correlation between the mass fraction and the velocity fluctuations:

$$\overline{Y_{ik} \underline{v}_k} \cong \overline{Y_{ik}} \overline{\underline{v}_k}. \quad (139)$$

Substituting this relation into (93) gives:

$$\begin{aligned} & \frac{\partial}{\partial t} (\varepsilon \alpha_k \langle \rho_k \rangle_k \overline{Y_{ik}^k}) + \nabla \cdot (\varepsilon \alpha_k \langle \rho_k \rangle_k \overline{Y_{ik}^k} \overline{\underline{v}_k}^k) \\ &= \nabla \cdot (D_{ik} \nabla (\varepsilon \alpha_k \langle \rho_k \rangle_k \overline{Y_{ik}^k})) + \Gamma_k Y_{ik}^\Gamma + \Sigma_{ik} + S_{ik}. \end{aligned} \quad (140)$$

This equation can be compared to the following one derived by [24] rewritten with our notations:

$$\begin{aligned} & \frac{\partial}{\partial t} (\varepsilon \alpha_k \langle C_{ik} \rangle_k) + \nabla \cdot (\varepsilon \alpha_k (\langle C_{ik} \rangle_k \langle \underline{v}_k \rangle_k + \langle C'_{ik} \underline{v}'_k \rangle_k)) \\ &= \frac{\Gamma_k}{\langle \rho_k \rangle_k} \langle C_{ik} \rangle_k + \nabla \cdot (D_{ik} [\nabla (\varepsilon \alpha_k \langle C_{ik} \rangle_k) + \varepsilon \alpha_k \underline{\tau}_{ik}]) \\ &+ \varepsilon \alpha_k K a_{Ik} (\langle C_{ik} \rangle_k - \langle C_{ik} \rangle_{k0}) + \varepsilon \alpha_k \langle r_{ik} \rangle_k. \end{aligned} \quad (141)$$

This comparison shows that  $\langle C_{ik} \rangle_k = \langle \rho_k \rangle_k \overline{Y_{ik}^k}$  (mass of species  $i$  per unit volume of phase  $k$ ),  $S_{ik} = \varepsilon \alpha_k \langle r_{ik} \rangle_k$  and  $\Sigma_{ik} = \varepsilon \alpha_k K a_{Ik} (\langle C_{ik} \rangle_k - \langle C_{ik} \rangle_{k0})$  where  $a_{Ik}$  is the volumetric interfacial area between phase  $k$  and the other phases and  $K$  is a mass transfer coefficient.  $\langle C_{ik} \rangle_{k0}$  denotes the concentration value at the interface with the other phase. Tardy [22] neglects this term as well as the dispersion term  $\langle C'_{ik} \underline{v}'_k \rangle_k$  and the tortuosity vector for the species  $\underline{\tau}_{ik}$ .

## 6.3 Simplification of the enthalpy balance equation

Zhang and Jiao [25] start from the multiphase model derived from [4] and transform it to a multiphase multicomponent mixture model by summing the equations on the different phases. Their model is used later in the channels of PEMFC by [26]. Here, we present the simplifications made by these authors, starting from our enthalpy balance equations (130) and (131). The enthalpy balance equation for phase  $k$  retained by [25] has the following form:

$$\begin{aligned} & \frac{\partial}{\partial t} (\varepsilon \alpha_k \langle \rho_k \rangle_k \overline{h_k^k}) + \nabla \cdot (\langle \rho_k \rangle_k \overline{h_k^k} \langle \underline{v}_k \rangle_k) \\ &= \nabla \cdot (\alpha_k k_k^{eff} \nabla T) + Q_k \end{aligned} \quad (142)$$

where  $\langle \underline{v}_k \rangle_k$  denotes the filtration velocity defined by (135). The comparison of (142) with our equation (130) shows the simplifying assumptions made by these authors. First of all, they adopt the thermal equilibrium assumption given by (11), hence, the phase-averaged temperatures are all equal to the mean temperature  $T$  for the medium. Secondly, all the diffusion and dispersion effects are modelled collectively by introducing an effective conductivity  $k_k^{eff}$ :

$$\begin{aligned} \nabla \cdot (\alpha_k k_k^{eff} \nabla T) &= \nabla \cdot \left( (k_k \underline{I} + \underline{k}_k^d) \cdot (\varepsilon \alpha_k \nabla \langle T_k \rangle_k + \underline{v}_k) \right) \\ &\text{by definition of } k_k^{eff}. \end{aligned} \quad (143)$$

Thirdly, the term  $Q_k$  in (142) models, collectively all the remaining terms in our equation (130):

$$\begin{aligned} Q_k &= \Gamma_k h_k^\Gamma + q_{kf} + q_{ks} + \varepsilon \alpha_k \langle r_k h_k^r \rangle_k \\ &+ \frac{\partial}{\partial t} (\varepsilon \alpha_k \langle p_k \rangle_k) + \varepsilon \alpha_k \overline{\underline{v}_k}^k \cdot \nabla \langle p_k \rangle_k + q''_{kf} + q''_{ks}. \end{aligned} \quad (144)$$

Summing the equations (142) on the different phases, including the solid phase  $s$ , the following equation is obtained:

$$\begin{aligned} & \frac{\partial}{\partial t} \left( (1 - \varepsilon) \rho_s h_s + \varepsilon \sum_{k \neq s} \alpha_k \rho_k h_k \right) + \nabla \cdot \left( \sum_{k \neq s} \rho_k h_k \langle \underline{v}_k \rangle_k \right) \\ &= \nabla \cdot (k_{eff} \nabla T) + Q \end{aligned} \quad (145)$$

with:

$$k_{eff} \stackrel{\text{def}}{=} \sum_{k \neq s} \alpha_k k_k^{eff} \text{ and } Q \stackrel{\text{def}}{=} \sum_{k \neq s} Q_k \quad (146)$$

Posing:

$$\begin{aligned} \rho h &\stackrel{\text{def}}{=} \sum_{k \neq s} \alpha_k \rho_k h_k \sum_k \rho_k h_k \langle \underline{v}_k \rangle_k \\ &= \sum_k \lambda_k h_k \rho \underline{v} + h_k \underline{j}_k \stackrel{\text{def}}{=} \gamma_h \rho h \underline{v} + \sum_k h_k \underline{j}_k \end{aligned} \quad (147)$$

where  $\lambda_k$  is the phase  $k$  mobility,  $\underline{j}_k$  is a diffusive flux due to the difference between the phases' velocities and  $\gamma_h$  is a correction factor for enthalpy convection defined by:

$$\lambda_k \stackrel{\text{def}}{=} \frac{K_{rk}}{v_k} v \rho_k \langle \underline{v}_k \rangle_k = \lambda_k \rho \underline{v} + \underline{j}_k \gamma_h \stackrel{\text{def}}{=} \frac{\rho \sum_{k \neq s} \lambda_k h_k}{\rho h} \quad (148)$$

where  $v_k$  and  $v$  denote the kinematic viscosities of the phase  $k$  and the mixture respectively.  $\rho$ ,  $\underline{v}$  and  $h$  denote the density, center of mass velocity, and enthalpy of the gas-liquid mixture:

$$\rho \stackrel{\text{def}}{=} \sum_k \alpha_k \rho_k \quad \rho \underline{v} \stackrel{\text{def}}{=} \sum_k \rho_k \langle \underline{v}_k \rangle_k. \quad (149)$$

Introducing (147) and (149) into (145), the equation for the mixture enthalpy reads:

$$\begin{aligned} & \frac{\partial}{\partial t} ((1 - \varepsilon)\rho_s h_s + \varepsilon\rho h) + \nabla \cdot (\gamma_h \rho h \underline{v}) \\ &= \nabla \cdot \left( k_{\text{eff}} \nabla T - \sum_k h_k \underline{j}_k \right) + Q \end{aligned} \quad (150)$$

Zhang *et al.* [27] as well as Tardy [22] retain only a two-phase version of the mixture temperature:

$$\begin{aligned} & \frac{\partial}{\partial t} \left( \sum_{k=L,G} \varepsilon \alpha_k \langle \rho_k \rangle_k C_{p,k} T \right) + \nabla \cdot \left( \sum_{k=L,G} \varepsilon \alpha_k \langle \rho_k \rangle_k C_{p,k} T \overline{\underline{v}}_k \right) \\ &= Q + \nabla \cdot (\varepsilon k_{\text{eff}} \nabla T). \end{aligned} \quad (151)$$

## 7 Conclusions

This paper gives a complete derivation of the average equations governing the two-phase multicomponent flows in porous media. The targeted application is the proton exchange membrane fuel cells. As we consider the fuel cells working at temperatures below 100 °C (typically 80 °C), water exists in gas and liquid phases in the interior of the PEMFC (porous layers and bipolar plates). All the equations have been derived for liquid and gas masses, species masses, momenta of the two phases, as well as the different forms of energy and entropy. The simplified versions of these equations currently used in PEMFC models are given in the last section.

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