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Heat and mass transfer in wet porous media in presence of evaporation–condensation

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Abstract—The modelling of heat and mass transfer in wet porous media in the presence of evaporationcondensation is revisited by using the homogenization method of asymptotic expansions for periodic structures. In order to produce the 'upscaled' equations for the continuum equivalent to the porous medium, we start from the pore level. At this scale the physics is described by convection and Fick's molecular diffusion coupled with heat transfer. The phase change process is incorporated into the analysis. The main advantage of the method is to use a systematic, rigorous and unified treatment to provide a general comprehension of all the interactions involved by the different heat and mass transfers. Four characteristic selected models are carried out. Their domains of validity are determined in function of the relative weight of the different phenomena in presence. Comparison with other models in the literature is presented. It appears that some of them exhibit a similar structure. In particular, the continuous passage between the different macroscopic models is investigated. Finally, the condition for a non-homogenizable situation, i.e., when it is impossible to find a macroscopic equivalent description is also addressed. © 1998 Elsevier Science Ltd. All rights reserved.

1. INTRODUCTION

Modelling simultaneous heat and mass transfers in porous media is of growing interest in a wide range of engineering domains, for meteorologists, soil scientists, agronomists or ecologists. Such phenomena are frequently encountered in industrial operations, including tertiary oil recovery practice, geothermal development, civil engineering, energy storage and energy conversion. For example, knowledge of the simultaneous transfer of heat and moisture in the uppermost soil layers is of great practical importance. The subject also concerns engineers interested in thermal transfer in porous or fissured media in connection with such problems as oil and geothermal extraction, exploration of the heat of hot and dry rocks (HDR) or nuclear waste disposal in geological formations, etc.

Heat and moisture transfers in wet porous media are coupled in a complicated way. On the one hand, water moves under the action of gravity and pressure gradient whilst the vapor phase moves by diffusion caused by a gradient of vapor density. On the other hand, heat is transported by conduction, radiation and convection. It is commonly known from the previous works by Krischer and Kroll [25], Philip and de Vries [27], de Vries [16, 18], that water movement through unsaturated porous media is often caused by a temperature gradient. Water evaporates from hot regions and moves across the gas-filled pores by diffusion and condenses on the cold region thus releasing its latent heat of vaporization. Consequently, the contribution of the vapor diffusion in the air-filled pores and its induced 'latent heat transport' has to be incorporated into the modelling.

A phenomenological theory of combined heat and moisture transfer in porous media was previously established by de Vries [16, 18] and Philip and de Vries [27]. Commonly known as the de Vries 'mechanistic' model, its practical usefulness is widely recognized in describing the simultaneous heat and moisture transfer within a wide range of porous media. Applying balance equations yields to the coupled system

$$C\frac{\partial T}{\partial t} = \nabla \cdot ((\lambda + L_{\nu}D_{T\nu})\nabla T) + \nabla \cdot (L_{\nu}D_{\partial\nu}\nabla\theta_{j})$$
(1a)

$$\frac{\partial \theta_{l}}{\partial t} = \nabla \cdot ((D_{\mathrm{TV}} + D_{\mathrm{TI}})\nabla T) + \nabla \cdot ((D_{\theta \mathrm{V}} + D_{\theta \mathrm{I}})\nabla \theta_{\mathrm{I}})$$

(1b)

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NOMENCLATURE

	10112110
A^{v}, B^{s}	$, B^{l}, B^{g}, P^{l}_{e}, P^{v}_{e}, P^{g}_{e}, N_{v}, N_{L_{v}}, N^{gl}, N^{gs},$
$N^{\rm ls}, M$	dimensionless numbers
$(c_{\rm p})_{\rm g},($	$(c_{p})_{l}, (c_{p})_{s}$ gas, liquid and solid heat
	capacity, respectively $[J kg^{-1} K^{-1}]$
D	binary air-vapor diffusion coefficient
	$[m^2 s^{-1}]$
D_{ii}^*	macroscopic (or effective) diffusion
	tensor $[m^2 s^{-1}]$
ERV	elementary representative volume
K _i , K _e	permeability tensors of the water and
	the gas, respectively $[m s^{-1}]$
1	characteristic length of the ERV (or
	the periodic cell) [m]
L	characteristic macroscopic length [m]
$L_{\rm v}$	latent heat of vaporization [J kg ⁻¹]
$M_{ m g}$	molar mass of the gas phase [kg mol ^{-1}]
$n_{\rm g}, n_{\rm l},$	$n_{\rm s}$ gas, liquid and solid porosity,
	respectively [dimensionless]
N_i^{g}, N	${}^{1}_{i}, N^{s}_{i}$ unit outward vector to Ω_{g}, Ω_{l} and
	$\Omega_{\rm s}$, respectively
$P_{\rm g}, P_{\rm l}$	gas and water pressure, respectively
	[Pa]
$q_{\mathrm{v}\Gamma_{\mathrm{gl}}}$	vapor source per unit volume at the
	gas-liquid interface [kg m ⁻³ s ⁻¹]
R	universal gas constant [J mol ⁻¹ K ⁻¹]
t	time [s]
$T_{\rm g}, T_{\rm l},$, $T_{\rm s}$ gas, liquid and solid temperature,
	respectively [K]
$v_{g_i}^{0eff}$	macroscopic (or effective) velocity of
0.07	the gaseous phase $[m s^{-1}]$
v_{li}^{0eff}	macroscopic (or effective) velocity of
	the liquid phase $[m s^{-1}]$
$v_{\rm a}, v_{\rm g},$	$v_{\rm I}, v_{\rm v}$ air, gas, liquid and vapor

velocity, respectively $[m s^{-1}]$

- v_{p} 'evaporation' velocity at the gas-liquid interface [m s⁻¹]
- w gas-liquid interface velocity $[m s^{-1}]$
- x macroscopic (or slow) space variable (dimensionless)
- X physical space variable [m]
- y microscopic (or fast) space variable (dimensionless).

Greek symbols

- $\Gamma_{gl}, \Gamma_{gs}, \Gamma_{is}$ gas-liquid, gas-solid, liquidsolid boundary, respectively
- ε homogenizaton parameter [dimensionless]
- $\lambda_{g}, \lambda_{l}, \lambda_{s}$ gas, liquid and solid thermal conductivity, respectively $[J m^{-1} K^{-1} s^{-1}]$
- $\lambda_{lij}^*, \lambda_{sij}^*$ macroscopic (or effective) conductivity tensor of the liquid and solid phase, respectively $[J m^{-1} K^{-1} s^{-1}]$
- ξ, χ pore vector fields
- $ho_{\rm s},
 ho_{\rm a},
 ho_{\rm v},
 ho_{\rm l}$ solid, air, vapor and liquid mass density, respectively [kg m⁻³]
- ω_{a}, ω_{v} air and vapor mass fraction, respectively (dimensionless)
- Ω period cell
- $|\Omega|$ total volume of the periodic cell [m³]
- $\Omega_i, \Omega_s, \Omega_g$ parts of the period occupied by the liquid, solid and gas, respectively $[m^3]$.

where

- ∇ , ∇ stand for the gradient and the divergence operator, respectively
- D_{TV} , D_{TI} are the thermally induced diffusivities of vapor and liquid, respectively $[\text{m}^2 \text{ s}^{-1} \text{ K}^{-1}]$
- $D_{\theta V}$, $D_{\theta 1}$ are the isothermal diffusivities of vapor and liquid, respectively $[m^2 s^{-1}]$
- θ_1 is the volumetric water content [dimensionless]
- *T* is the temperature [K]
- λ is the 'hypothetical' thermal conductivity [J m⁻¹ K⁻¹ s⁻¹]
- C is the volumetric heat capacity $[J m^{-3} K^{-1}]$
- L_v is the latent heat of vaporization [J kg⁻¹]
- *t* is the time [s].

Furthermore, generalized diffusivities D_{θ} and D_{T} can be defined as follows

$$D_{\theta} = D_{\theta \mathsf{v}} + D_{\theta \mathsf{l}} \tag{2a}$$

$$D_{\mathrm{T}} = D_{\mathrm{TV}} + D_{\mathrm{TI}}.$$
 (2b)

The main advantages of the de Vries approach can be attributed to the fact that theoretical expressions for the generalized diffusivities D_{θ} and $D_{\rm T}$ for moisture transport due to a moisture gradient and to a temperature gradient, respectively, are available from only two independent variables: the temperature Tand the water volumic moisture content θ_1 . In [30], Whitaker presents the first important temptative to introduce a rigorous derivation of the model by volume averaging the pore scale equations.

Various laboratory and field tests were conducted to check the applicability of the de Vries and the Philip and de Vries model (Crausse [10], Crausse *et al.* [11], Daïan [12], [13], de Vries [17], Hadas [19], van der Kooi [24], Jury [23] cited in de Vries [18], Horton and Wierenga [21], Moyne *et al.* [26], Shepherd and Wiltshire [29]). The de Vries model predicts quite accurately the heat transfer under stationary conditions. However, fluctuating thermal conditions yield underestimation. Thus, some adjustment factors proved to be necessary to obtain agreement between theory and experiment (e.g., an enhancement factor— Hadas [19], Shepherd and Wiltshire [29]).

van der Kooi [24] studied heat and moisture in cellular concrete roofs. He found that the behaviour of cellular concrete slabs could be predicted quite accurately by the Philip and de Vries theory. However, some correction factors (based on successive approximations) were required for the macroscopic diffusivities D_0 and D_T to agree with the numerical simulations.

In his doctoral dissertation, Jury ([23] cited in de Vries [18]) analyses how the de Vries and Philip model is related to the flux equations given by the thermodynamics of irreversible processes (TIP). It comes out from his experimental data (see the comments in Hamburger [20]) that the Philip's and de Vries's model underestimates the water flux about five orders of magnitude.

In order to avoid this underestimation, Moyne *et al.* [26] apply the volume averaging method to the grain scale description and obtained the following upscaled continuum equivalent modelling

$$\langle \rho c_{\rm p} \rangle \frac{\partial \langle T \rangle}{\partial t} = \frac{\partial}{\partial x_i} \left(\lambda_{ij} \frac{\partial \langle T \rangle}{\partial x_j} \right) - \Delta h_{\rm v} \langle \dot{m} \rangle \quad (3a)$$

$$\rho_{g} \frac{\partial \langle \omega_{v} \rangle^{g}}{\partial t} = \frac{\partial}{\partial x_{i}} \left(\rho_{g} D f_{ij} \frac{\partial \langle \omega_{v} \rangle^{g}}{\partial x_{j}} \right) + \langle \dot{m} \rangle \quad (3b)$$

where

- ⟨T⟩ is the volume average of the temperature defined on the elementary representative volume (REV) [K]
- $\langle \omega_v \rangle^g$ is the intrinsic phase average of the vapor mass fraction ω_v over the gaseous phase volume [dimensionless]
- \$\langle m \rangle\$ is the mass of evaporated water per unit volume and unit time [kg m⁻³ s⁻¹]
- λ_{ij} is the 'true' effective thermal conductivity [J m⁻¹ k⁻¹ s⁻¹]
- Δh_{ν} designs the latent heat of water vaporization [J kg⁻¹]
- $\langle \rho c_p \rangle$ is the volume average of the volumic heat capacity [J m⁻³ K⁻¹].

As first suggested by Philip and de Vries [16, 18, 27] a resistance factor f_{ij} is incorporated into the analysis to model the influence of the solid and the liquid phases. Hadas [19] applied the de Vries model to evaluate the amount of energy moved by vapor transfer at the soil surface. It was found that the transfer of heat by vapor under steady state conditions could be accurately predicted by the theory in case of permanent transfers. However, under fluctuating state conditions some corrections by 'enhancement factors'

proved to be necessary to obtain closer agreement between theoretical and measured values.

Using the cylindrical probe method described by de Vries [14, 15], Horton and Wierenga [21] consider a compacted sand at a given volumetric water content in order to measure its thermal conductivity. According to the de Vries method [17], the accordance between the experimental and calculated data was relatively good.

By means of the Philip and de Vries approach [16, 27], Shepherd and Wiltshire [29] investigate the case of an asymptotically steady state in soils for which an analytical approach is available. The method consists in approximating the Philip and de Vries equations [16, 27] by an associated system of linear differential equations that can be solved explicitly. The solution is then applied to conditions prevailing in arid soil. Enhancement factors are here also introduced for a better checking of the theory. The reader is referred to [29] for more information about these works.

Neither of the presented theoretical approaches take into account the all complexity of the interactions involved by the coupled heat and moisture transfers. The aim of this paper is to present new mathematical models for heat and mass transfer in porous media. For this purpose we use the method of multiple scale expansions to upscale the description at the pore scale to the macroscopic scale. For this purpose we assume the existence of an elementary representative volume (ERV) that is small in regard of the macroscopic characteristic length of the heat and mass transfer. For simplicity, we assume a similar macroscopic length for the heat and the mass transfer, respectively. The reader is referred to Bachmat and Bear [6] and Anguy [1] for the definition of the ERV and the determination of its characteristic size.

This paper is organized as follows. Section 2 is devoted to a general presentation of the physics at the pore scale and to a brief survey of the homogenization method (Bensoussan et al. [7]; Sanchez-Palencia [28], Auriault [4]). The homogenization technique is then applied in Section 3 to the determination of the macroscopic coupled heat and mass transfer equations. Under certain conditions in relation to the order magnitude of the different dominating phenomena, it is shown that the mass and the heat transfer equations can be solved separately. Considering the mass transfer problem, four different cases are presented that yield four different macroscopic models. The domains of validity of the different models are clearly shown and the continuous passage from a model to the others is investigated. Finally, we present the conditions for which homogenization is not possible, i.e., when it is impossible to find a macroscopic equivalent continuum. A more detailed analysis and other macroscopic models can be found in Bouddour [9].

2. THE DESCRIPTION AT THE PORE SCALE

Numerous heterogeneous porous media such as concrete, ceramic, rocks, etc., are constituted by a



Fig. 1. Macroscopic (a) and microscopic (b) views of a spatially periodic porous unsaturated medium. Two length scales are displayed.

single porosity system in which the dimension of the pore can vary widely. As recalled in the previous discussion, the necessary and essential condition for the homogenization method to be applied to such media is the existence of an elementary representative volume (ERV) of the medium, which is small in comparison to the macroscopic volume. In periodic media, the period stands for the ERV. Let l be its characteristic length. Let L be the characteristic dimension of the studied phenomenon in the sample). The separation of scales condition is written

$$\varepsilon = \frac{l}{L} \ll 1 \tag{4}$$

where ε is the parameter of scale separation. The scale separation condition (4) enables us to use the doublescale asymptotic expansion technique. Under this condition, the macroscopic models to be obtained are intrinsic to the porous medium and to the phenomenon. They are independent of the macroscopic boundary conditions. In the course of the analysis, two non-dimensional space variables will be used $\mathbf{x} = (\mathbf{X}/L)$ and $\mathbf{y} = (\mathbf{X}/l)$ where \mathbf{X} is the physical space variable. Each unknown of a given boundary value problem appears as a function of these two dimensionless space variables. The variable \mathbf{x} is the macroscopic (or slow) space variable and \mathbf{y} is the microscopic (or fast) space variable.

We consider a periodic porous medium (see Fig. 1) with the space period Ω . Ω_s , Ω_1 and Ω_g are the domains occupied by the solid phase (s), the liquid (l) and the gas phase (g) within the period, respectively. Γ_{gl} , Γ_{gs} and Γ_{ls} are the gas–liquid, the gas–solid and the liquid–solid interfaces, respectively. The solid part Ω_s is assumed to be rigid. The gas phase is a mixture of two components : the air (a) and the vapor (v).

One of the most important steps in all homogenization processes is to estimate the homogenization parameter ε . However, this problem is out of the scope of the present paper. It must be stressed, that the adequate macroscopic model strongly depends on the scale separation. For the simplicity of the presentation the following separation of scale is adopted: $\varepsilon = (l/L) \approx 10^{-2}$ (see Bloch [8]). Quite different values of ε are available, depending on the macroscopic boundary value problem. For example, when studying nuclear waste disposals in geological formation, Hosanski *et al.* [22], consider the mass and heat transfer dissipated by waste radioactive within fracture granitic rocks. The authors model the medium as a rectangular and periodic, single porosity system, the characteristic length of which yields the following geometrical separation of scale: $\varepsilon \approx 10^{-7}$.

In the following analysis, the simultaneous processes of heat and mass transfer are examined with respect to different dominating phenomena. We assume no hysteresis and we neglect heat radiation transfer, gravity and physicochemical interactions between the solid and the fluids.

We start from the pore level where the equation which governs the vapor mass fraction ω_v is written in the form :

$$\rho_{g}\frac{\partial\omega_{v}}{\partial t} + \rho_{g}v_{gi}\frac{\partial\omega_{v}}{\partial X_{i}} - \frac{\partial}{\partial X_{i}}\left(\rho_{g}D\frac{\partial\omega_{v}}{\partial X_{i}}\right) = 0 \qquad (5)$$

where

- ρ_{g} is the mass density of the gas
- v_{gi} is the velocity of the gas
- D is the binary air-vapor diffusion coefficient assumed as isotropic.

Moreover, the velocity of the air-vapor mixture is written:

$$v_{gi} = \omega_{\rm v} v_{\rm vi} + \omega_{\rm a} v_{\rm ai} \tag{6}$$

where

- v_{vi} and v_{ai} are the velocities of the vapor and the air in the gaseous phase, respectively
- the air mass fraction is given by

$$\omega_{\rm a} = 1 - \omega_{\rm v}.\tag{7}$$

On the other hand, the heat transfer inside each phase, gas (g), liquid (1) and solid (s), is governed by conduction and convection. Hence, in the liquid phase and the gaseous phase the heat transfer is described by the following microscale equation :

$$(\rho c_{p})_{\beta} \frac{\partial T_{\beta}}{\partial t} + (\rho c_{p})_{\beta} v_{\beta i} \frac{\partial T_{\beta}}{\partial X_{i}} - \frac{\partial}{\partial X_{i}} \left(\lambda_{\beta} \frac{\partial T_{\beta}}{\partial X_{i}} \right) = 0$$
(8)

where

- $\beta = \{1, g\}$ stands for the liquid and the gas phase
- T_{β} is the temperature of the phase β
- $v_{\beta i}$ is the velocity of the phase β
- $(\rho c_p)_{\beta}$ is the volumic heat capacity of the phase β
- λ_{β} is the thermal conductivity of the phase β assumed as isotropic.

In the solid phase the heat transfer is governed by conduction only

$$(\rho c_{\rm p})_{\rm s} \frac{\partial T_{\rm s}}{\partial t} - \frac{\partial}{\partial X_i} \left(\lambda_{\rm s} \frac{\partial T_{\rm s}}{\partial X_i} \right) = 0. \tag{9}$$

We will show that the temperature is a constant on the period for the investigated situations. Therefore, the thermodynamic equilibrium prevails on both the gas-solid Γ_{gs} and gas-liquid Γ_{gl} interfaces. Then, the gas density ρ_{g} , the gas pressure P_{g} and the gas temperature T_{g} are related by the gas state equation :

$$\rho_{\rm g} = \frac{M_{\rm g} P_{\rm g} |\Omega_{\rm g}|}{R T_{\rm g}} \quad \text{in } \Omega_{\rm g} \tag{10}$$

where

where

- $M_{\rm g}$ is the molar mass of the gas phase
- $|\Omega_{g}|$ is the volume of the gaseous phase
- R is the universal gas constant.

The preceding set of equations must be completed by proper boundary conditions on Γ_{gl} , Γ_{gs} and Γ_{ls} . Let us first introduce the conditions on the gas-liquid interface Γ_{gl} .

We assume the insolubility of air in water, that gives:

$$v_{\rm ai}N_i^{\rm g} = 0 \quad \text{on } \Gamma_{\rm gl} \tag{11}$$

where N_i^{g} represents the outward unit normal to Ω_{g} .

Let $v_{pi} = \omega_v v_{vi}$ be the 'evaporation' velocity at the gas-liquid interface. Then, introducing relation (11), the continuity of the flux vapor can be written as follows:

$$\rho_{\rm a} v_{\rm pi} N_i^{\rm g} = -\rho_{\rm g} D \frac{\partial \omega_{\rm v}}{\partial X_i} N_i^{\rm g} \quad \text{on } \Gamma_{\rm gl} \tag{12}$$

where ρ_a is the mass density of the air phase.

The mass conservation on Γ_{gl} is written

$$\rho_{\rm I}(v_{\rm li} - w_i)N_i^{\rm g} = \rho_{\rm g}(v_{\rm pi} - w_i)N_i^{\rm g} \tag{13}$$

- w_i is the gas-liquid interface velocity
- ρ_1 and v_{1i} are the mass density and the velocity of the liquid phase (water), respectively.

On Γ_{gl} , we assume the continuity of the temperature (14) and the heat flux verifies (15):

$$T_{\rm g} = T_1 \tag{14}$$

$$-\lambda_{g}\frac{\partial T_{g}}{\partial X_{i}}N_{i}^{g} = -\lambda_{l}\frac{\partial T_{l}}{\partial X_{i}}N_{i}^{g} + \rho_{g}DL_{v}\frac{\partial\omega_{v}}{\partial X_{i}}N_{i}^{g} \quad (15)$$

where L_{ν} is the latent heat of vaporization which depends only on the temperature of water.

On the gas–solid interface Γ_{gs} , the boundary conditions are:

$$\rho_{\rm g} D \frac{\partial \omega_{\rm v}}{\partial X_i} N_i^{\rm g} = 0 \tag{16}$$

$$T_{\rm g} = T_{\rm s} \tag{17}$$

$$\lambda_{g} \frac{\partial T_{g}}{\partial X_{i}} N_{i}^{g} = \lambda_{s} \frac{\partial T_{s}}{\partial X_{i}} N_{i}^{g}.$$
(18)

Finally on the liquid-solid interface Γ_{ls} we have :

$$T_1 = T_s \tag{19}$$

$$\lambda_1 \frac{\partial T_1}{\partial X_i} N_i^{\mathfrak{l}} = \lambda_s \frac{\partial T_s}{\partial X_i} N_i^{\mathfrak{l}}$$
(20)

where N_i^1 represents the outward unit normal for phase (1).

The above system of equations (5), (8), (9), (12), (13), (15), (18), (20) introduces thirteen dimensionless numbers.

In the solid volume Ω_s :

$$B^{s} = \frac{\left| \left(\rho c_{p} \right)_{s} \frac{\partial T_{s}}{\partial t} \right|}{\left| \frac{\partial}{\partial X_{i}} \left(\lambda_{s} \frac{\partial T_{s}}{\partial X_{i}} \right) \right|} \quad \text{(inverse of a Fourier number)}.$$

(21)

In the liquid volume Ω_{l} ,

$$B^{1} = \frac{\left| (\rho c_{p})_{1} \frac{\partial T_{i}}{\partial t} \right|}{\left| \frac{\partial}{\partial X_{i}} \left(\lambda_{1} \frac{\partial T_{1}}{\partial X_{i}} \right) \right|} \quad \text{(inverse of a Fourier number)}$$
(22)

$$P_{e}^{l} = \frac{\left| (\rho c_{p})_{l} v_{li} \frac{\partial T_{l}}{\partial X_{i}} \right|}{\left| \frac{\partial}{\partial X_{i}} \left(\lambda_{l} \frac{\partial T_{l}}{\partial X_{i}} \right) \right|} \quad (Péclet number).$$
(23)

In the gas volume Ω_{g} ,

(26)

(28)

$$A^{\mathrm{v}} = \frac{\left|\rho_{\mathrm{g}}\frac{\partial\omega_{\mathrm{v}}}{\partial t}\right|}{\left|\frac{\partial}{\partial X_{i}}\left(\rho_{\mathrm{g}}D\frac{\partial\omega_{\mathrm{v}}}{\partial X_{i}}\right)\right|}$$

(inverse of a massic Fourier number) (24)

$$P_{e}^{v} = \frac{\left|\rho_{g} v_{gi} \frac{\partial \omega_{v}}{\partial X_{i}}\right|}{\left|\frac{\partial}{\partial X_{i}} \left(\rho_{g} D \frac{\partial \omega_{v}}{\partial X_{i}}\right)\right|} \quad (Péclet number) \quad (25)$$

$$g = \frac{\left|\rho_{g} c_{pg} \frac{\partial T_{g}}{\partial t}\right|}{\left|\frac{\partial}{\partial X_{i}} \left(\lambda_{g} \frac{\partial T_{g}}{\partial X_{i}}\right)\right|} \quad (inverse of a Fourier number)$$

$$P_{c}^{g} = \frac{\left| \rho_{g} c_{pg} v_{gi} \frac{\partial T_{g}}{\partial X_{i}} \right|}{\left| \frac{\partial}{\partial X_{i}} \left(\lambda_{g} \frac{\partial T_{g}}{\partial X_{i}} \right) \right|} \quad (Péclet number).$$
(27)

On the gas–liquid interface Γ_{gl} ,

$$N_{\rm p} = \frac{|\rho_{\rm a} v_{\rm pi} N_i^{\rm g}|}{\left|\rho_{\rm g} D \frac{\partial \omega_{\rm v}}{\partial X_i} N_i^{\rm g}\right|} \quad (\text{vapor flux/diffusion flux})$$

$$N_{L_{\rm v}} = \frac{\left| \rho_{\rm g} D L_{\rm vi} \frac{\partial \omega_{\rm v}}{\partial X_{\rm i}} N_{\rm i}^{\rm g} \right|}{\left| \lambda_{\rm i} \frac{\partial T_{\rm i}}{\partial X_{\rm i}} N_{\rm i}^{\rm g} \right|}$$

(phase change flux/thermal flux). (29)

From characteristic values for air and water and the adopted value of ε , we get

$$N^{g_1} = \frac{\lambda_g}{\lambda_1} = O(\varepsilon). \tag{30}$$

In case of soil samples, we have on the gas-solid interface $\Gamma_{\rm gs}$:

$$N^{\rm gs} = \frac{\lambda_{\rm g}}{\lambda_{\rm s}} = O(\varepsilon) \tag{31}$$

and on the liquid–solid interface Γ_{ls} :

$$N^{\rm ls} = \frac{\lambda_{\rm s}}{\lambda_{\rm l}} = O(1). \tag{32}$$

Finally, equation (13) introduces the following ratio

$$M = \frac{|\rho_{g}(v_{pi} - w_{i})N_{i}^{g}|}{|\rho_{1}(v_{1i} - w_{i})N_{i}^{g}|}.$$
(33)

For the existence of a macroscopic model (Section 3), it is necessary to assume that the interface Γ_{gl} is slowly

varying. More precisely, w_i is supposed to be very small relatively to the vapor velocity v_{v_i} . We take:

$$\left|\frac{v_{vi}N_i^g}{w_iN_i^g}\right| = O(\varepsilon^{-3}). \tag{34}$$

Furthermore, the liquid velocity v_{li} is assumed to be smaller by an ε -order of magnitude than the interfacial velocity w_i

$$\left|\frac{v_{li}N_i^g}{w_iN_i^g}\right| = O(\varepsilon). \tag{35}$$

Finally, we have

$$\left|\frac{\rho_{\mathbf{v}}}{\rho_{1}}\right| = O(\varepsilon^{3}). \tag{36}$$

Note that B^{s} , B^{l} , P_{e}^{l} , A^{v} , P_{e}^{v} , B^{g} , P_{e}^{g} are defined in the bulk of each phase whereas N_{p} , N_{Lv} , N^{gl} , N^{gs} , N^{ls} and M are surface dimensionless numbers. In the process of homogenization all the quantities will be normalized with respect to the characteristic length l, i.e., they will be changed into dimensionless variables using l as a reference length. Hence, the corresponding dimensionless space variable is \mathbf{y} (the microscopic variable) and the dimensionless numbers will be denoted with the subscript l. It must be stressed that all the quantities in front of the dimensionless numbers in the dimensionless equations are O(1). That makes the method of homogenization applicable. For simplicity, notations for dimensionless and physical quantities are similar.

3. THE MACROSCOPIC MODELS OF HEAT AND MASS TRANSFER IN POROUS MEDIA

The purpose of the analysis is to derive the macroscopic equivalent governing equations and the effective coefficients that describe the heat and mass transfer. Taking advantage of the small parameter ε , the vapor mass fraction ω_v , the mass density ρ_g , the temperature T_{α} of the phase $\alpha = \{s, l, g\}$, the 'evaporation' velocity v_{μ} , and the velocity $v_{\beta i}$ of the phase $\beta = \{l, g\}$ are expanded in ascending powers of ε :

$$\omega_{\mathbf{v}} = \omega_{\mathbf{v}}^{0}(\mathbf{x}, \mathbf{y}, t) + \varepsilon^{1} \omega_{\mathbf{v}}^{1}(\mathbf{x}, \mathbf{y}, t) + \varepsilon^{2} \omega_{\mathbf{v}}^{2}(\mathbf{x}, \mathbf{y}, t) + \cdots$$
(37)

$$\rho_{g} = \rho_{g}^{0}(\mathbf{x}, \mathbf{y}, t) + \varepsilon^{1} \rho_{g}^{1}(\mathbf{x}, \mathbf{y}, t) + \varepsilon^{2} \rho_{g}^{2}(\mathbf{x}, \mathbf{y}, t) + \cdots$$

$$T_{\alpha} = T_{\alpha}^{0}(\mathbf{x}, \mathbf{y}, t) + \varepsilon^{1} T_{\alpha}^{1}(\mathbf{x}, \mathbf{y}, t) + \varepsilon^{2} T_{\alpha}^{2}(\mathbf{x}, \mathbf{y}, t) + \cdots$$
(39)

$$v_{\beta i} = v_{\beta i}^{0}(\mathbf{x}, \mathbf{y}, t) + \varepsilon^{1} v_{\beta i}^{1}(\mathbf{x}, \mathbf{y}, t) + \varepsilon^{2} v_{\beta i}^{2}(\mathbf{x}, \mathbf{y}, t) + \cdots$$
(40)

$$v_{\mathrm{p}i} = v_{\mathrm{p}i}^0(\mathbf{x}, \mathbf{y}, t) + \varepsilon^1 v_{\mathrm{p}i}^1(\mathbf{x}, \mathbf{y}, t) + \varepsilon^2 v_{\mathrm{p}i}^2(\mathbf{x}, \mathbf{y}, t) + \cdots$$

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B

In the above expansions the ω_v^i , ρ_g^i , T_a^i , $v_{\beta i}^j$ and $v_{p i}^i$ are y-periodic and

$$\mathbf{x} = \varepsilon \mathbf{y}.\tag{42}$$

For slow flow, the velocities v_{li} and v_{gi} are given by the Stokes equation. The upscaling process is presented elsewhere [2, 3]. We limit ourselves to the presentation of the results. For actual non-saturated porous media, the mechanical interaction between the two fluids seems to be negligible (Zarcone [31]). The velocity fields are given by

$$v_{\beta i}^{0} = -k_{\beta i j}(\mathbf{y}, t) \frac{\partial P_{\beta}^{0}}{\partial x_{i}} \quad P_{\beta}^{0} = P_{\beta}^{0}(\mathbf{x}, t).$$
(43)

The Darcy's fluxes are obtained by volume averaging

$$v_{\beta i}^{\text{oeff}} = \frac{1}{|\Omega|} \int_{\Omega_{\beta}} v_{\beta i}^{0} \, \mathrm{d}\Omega = -K_{\beta i j} \frac{\partial P_{\beta}^{0}}{\partial x_{j}} \quad \beta = 1, g \qquad (44)$$

where \mathbf{K}_{i} and \mathbf{K}_{g} are the permeability tensors of the water and the gas, respectively.

We now estimate the dimensionless numbers. Recall that some of them were determined in the preceding section. Some other ones are chosen in a way to investhe richest homogenizable tigate situation: $B_l^s = B_l^1 = B_l^g = O(\varepsilon^2)$ and $P_{el}^g = P_{el}^1 = O(\varepsilon)$. Consequently, we are left with solely four variable dimensionless parameters which in fact govern the heat and mass transfer process with evaporation/condensation. Four cases of interest corresponding to different orders of the dimensionless numbers are carried out. We will consider $A_l^{v} = O(\varepsilon^m), P_{el}^{v} = O(\varepsilon^n), N_{pl} = O(\varepsilon^p)$ $N_{L,l} = O(\varepsilon^q)$ with (m, n, p, q) = (2, 1, 2, 0),and (1, 1, 1, 0), (1, 0, 2, 1) and (2, 2, 2, 0). The preceding four combinations for (m, n, p, q) lead to four different equivalent macroscopic descriptions. The mass and the heat transfer problems can be investigated separately. We first investigate the four different models for vapor mass transfer. Next, we study the corresponding models for heat transfer. By means of the homogenization technique each formulation is presented in relation with the selected dimensionless numbers characterizing the phenomena. We thus obtain the applicability conditions of the different formulations as well as the different effective parameters characterizing the averaged properties of the medium at the macro scale.

3.1. The mass transfer model

Model 1: vapor mass transfer model by diffusionadvection and evaporation-condensation

In the first case, we consider $A_l^v = O(\varepsilon^2)$, $P_{el}^v = O(\varepsilon)$, $N_{pl} = O(\varepsilon^2)$ and $N_{L,l} = O(1)$. Equations (5), (10), (12), (13), (15) and (16) take the dimensionless form

$$\varepsilon^{2} \rho_{g} \frac{\partial \omega_{v}}{\partial t} + \varepsilon \rho_{g} v_{gi} \frac{\partial \omega_{v}}{\partial y_{i}} - \frac{\partial}{\partial y_{i}} \left(\rho_{g} D \frac{\partial \omega_{v}}{\partial y_{i}} \right) = 0 \quad \text{in } \Omega_{g}.$$
(45)

The gas state equation is given by

$$\rho_{\rm g} = \frac{M_{\rm g} P_{\rm g} |\Omega_{\rm g}|}{RT_{\rm g}} \quad \text{in } \Omega_{\rm g}. \tag{46}$$

The boundary conditions are written :

$$\varepsilon^2 \rho_a v_{pi} N_i^g + \rho_g D \frac{\partial \omega_v}{\partial y_i} N_i^g = 0 \quad \text{on } \Gamma_{gl}$$
 (47)

$$\rho_{\rm l}(\varepsilon v_{\rm li} - w_i)N_i^{\rm g} = \varepsilon^3 \rho_{\rm g}(\varepsilon^{-3}v_{\rm pi} - w_i)N_i^{\rm g} \quad \text{on } \Gamma_{\rm gl}$$
(48)

$$-\varepsilon\lambda_{g}\frac{\partial T_{g}}{\partial y_{i}}N_{i}^{g}+\lambda_{1}\frac{\partial T_{1}}{\partial y_{i}}N_{i}^{g}-\rho_{g}DL_{v}\frac{\partial \omega_{v}}{\partial y_{i}}N_{i}^{g}=0 \quad \text{on } \Gamma_{gl}$$
(49)

$$\rho_{\rm g} D \frac{\partial \omega_{\rm v}}{\partial y_i} N_i^{\rm g} = 0 \quad \text{on } \Gamma_{\rm gs}. \tag{50}$$

After introduction of the expansions in the dimensionless equations, successive boundary value problems are obtained at the different orders of ε . The detailed calculus is itemized in Appendix A (Section A-1).

The first order description is governed by the following macroscopic equation (A19)

$$n_{g}\rho_{g}^{0}\frac{\partial\omega_{v}^{0}}{\partial t} + \rho_{g}^{0}v_{gt}^{0\text{eff}}\frac{\partial\omega_{v}^{0}}{\partial x_{j}} - \frac{\partial}{\partial x_{i}}\left(D_{ij}^{*}\rho_{g}^{0}\frac{\partial\omega_{v}^{0}}{\partial x_{j}}\right) + \rho_{a}^{0}q_{v\Gamma_{gt}} = 0. \quad (A19)$$

The different effective parameters in (A19) are as follows:

the porosity of the gaseous phase is given by

$$n_{\rm g} = \frac{|\Omega_{\rm g}|}{|\Omega|} \tag{51}$$

• the tensor D_{ij}^* is the macroscopic (or effective) diffusion tensor

$$D_{ij}^{*} = \frac{1}{|\Omega|} \int_{\Omega_{s}} D\left(\frac{\partial \xi_{j}}{\partial y_{i}} + I_{ij}\right) d\Omega$$
 (52)

where ξ is defined in Appendix A (Section A-1).

• $q_{v\Gamma_{gi}}$ is the vapor source per unit volume defined as the volume average

$$q_{v\Gamma_{gl}} = \frac{1}{|\Omega|} \int_{\Gamma_{gl}} v_{pl}^0 N_l^g \, \mathrm{d}\mathbf{S} = -\frac{\rho_l}{\rho_g^0} \frac{\mathrm{d}}{\mathrm{d}t}(n_l)$$
$$= \frac{1}{|\Omega|} \frac{\rho_l}{\rho_g^0} \frac{R}{M_g} \frac{\mathrm{d}}{\mathrm{d}t} \left(\frac{\rho_g^0 T_g^0}{P_g^0}\right). \tag{53}$$

The mass transport in Model 1 is due to diffusionadvection with evaporation-condensation effects at the liquid-gas interface.

The vapor source $q_{v\Gamma_{gl}}$ which is linked to the variation of the water content can be connected at the first order of approximation to the gas state variables [see Appendix A, equation (A25) and (A28)]. Note that d/dt in equation (53) stands for the Lagrangian derivative. Furthermore, it can be shown that the effective diffusion tensor **D**^{*} is symmetric and positive definite. It classically depends on the molecular diffusion as well as the geometry of the cell period. Due to the considered value of the Péclet number, it is not dispersive (Auriault and Lewandoska [5]).

 $v_{gi}^{0\text{eff}}$ is the macroscopic (or effective) velocity of the gaseous phase already determined previously in (44).

Model 2: vapor mass transfer model by evaporationcondensation only

We consider now $A_l^{\nu} = O(\varepsilon)$, $P_{el}^{\nu} = O(\varepsilon)$, $N_{pl} = O(\varepsilon)$ and $N_{L,l} = O(1)$. The relative magnitude of the transient term is increased by an order of magnitude as well as the contribution of the vapor transfer on Γ_{gl} . The equations to be investigated are

$$\varepsilon \rho_{g} \frac{\partial \omega_{v}}{\partial t} + \varepsilon \rho_{g} v_{gi} \frac{\partial \omega_{v}}{\partial y_{i}} - \frac{\partial}{\partial y_{i}} \left(\rho_{g} D \frac{\partial \omega_{v}}{\partial y_{i}} \right) = 0 \quad \text{in } \Omega_{g}$$

(54)

$$\rho_{g} = \frac{M_{g} P_{g} |\Omega_{g}|}{R T_{g}} \quad \text{in } \Omega_{g}.$$
 (55)

The boundary conditions are written:

$$\varepsilon \rho_a v_{\rm pi} N_i^{\rm g} + \rho_{\rm g} D \frac{\partial \omega_{\rm v}}{\partial y_i} N_i^{\rm g} = 0 \quad \text{on } \Gamma_{\rm gl}$$
 (56)

$$\rho_1(\varepsilon v_{ii} - w_i)N_i^g = \varepsilon^3 \rho_g(\varepsilon^{-3} v_{pi} - w_i)N_i^g \quad \text{on } \Gamma_{gl}$$
(57)

$$-\varepsilon\lambda_{g}\frac{\partial T_{g}}{\partial y_{i}}N_{i}^{g}+\lambda_{l}\frac{\partial T_{l}}{\partial y_{i}}N_{i}^{g}-\rho_{g}DL_{v}\frac{\partial\omega_{v}}{\partial y_{i}}N_{i}^{g}=0 \quad \text{on } \Gamma_{gl}$$

$$\rho_g D \frac{\partial \omega_v}{\partial y_i} N_i^g = 0 \quad \text{on } \Gamma_{gs}.$$
⁽⁵⁹⁾

The process of homogenization yields to the macroscopic governing equation which consists of the balance of the transient term and the vapor source per unit volume and unit time:

$$n_{\rm g}\rho_{\rm g}^0 \frac{\partial \omega_{\rm v}^0}{\partial t} + \rho_{\rm a}^0 q_{\rm v\Gamma_{\rm gl}} = 0. \tag{60}$$

In this case the convective and diffusive terms are not present in the equivalent macroscopic behaviour at the first order of approximation. $q_{v\Gamma_{gl}}$ is defined by (53).

Model 3: vapor mass transfer model by advection

In order to see the competitive influence of advection, the Péclet number is increased by an order of magnitude whereas the dimensionless parameter N_{pl} related to the vapor flux and the heat flux at gasliquid interface is decreased, respectively. We take $A_l^{\vee} = O(\varepsilon), P_{el}^{\vee} = O(1), N_{pl} = O(\varepsilon^2)$ and $N_{L,l} = O(\varepsilon)$. The local equations are now written in the form

$$\varepsilon \rho_{g} \frac{\partial \omega_{v}}{\partial t} + \rho_{g} v_{gi} \frac{\partial \omega_{v}}{\partial y_{i}} - \frac{\partial}{\partial y_{i}} \left(\rho_{g} D \frac{\partial \omega_{v}}{\partial y_{i}} \right) = 0 \quad \text{in } \Omega_{g}$$
(61)

$$\rho_{g} = \frac{M_{g} P_{g} |\Omega|}{R T_{g}} \quad \text{in } \Omega_{g}. \tag{62}$$

The boundary conditions are

$$\varepsilon^2 \rho_a v_{pi} N_i^g + \rho_g D \frac{\partial \omega_v}{\partial y_i} N_i^g = 0 \quad \text{on } \Gamma_{gi}$$
 (63)

$$\rho_1(\varepsilon v_{1i} - w_i)N_i^g = \varepsilon^3 \rho_g(\varepsilon^{-3} v_{pi} - w_i)N_i^g \quad \text{on } \Gamma_{gl}$$
(64)

$$-\varepsilon\lambda_{g}\frac{\partial T_{g}}{\partial y_{i}}N_{i}^{g}+\lambda_{1}\frac{\partial T_{1}}{\partial y_{i}}N_{i}^{g}-\varepsilon\rho_{g}DL_{v}\frac{\partial\omega_{v}}{\partial y_{i}}N_{i}^{g}=0\quad\text{on }\Gamma_{g}$$

$$\rho_{\rm g} D \frac{\partial \omega_{\rm v}}{\partial y_i} N_i^{\rm g} = 0 \quad \text{on } \Gamma_{\rm gs}. \tag{66}$$

After applying the homogenization procedure we obtain the macroscopic governing equation that consists of the balance of the transient and the advective terms

$$n_{\rm g}\rho_{\rm g}^0 \frac{\partial \omega_{\rm v}^0}{\partial t} + \rho_{\rm g}^0 v_{\rm gi}^{\rm 0eff} \frac{\partial \omega_{\rm v}^0}{\partial x_i} = 0$$
 (67)

 $v_{gi}^{0\text{eff}}$ is the macroscopic (or effective) velocity of the gaseous phase already defined previously in (44). The appropriate local boundary value problem for a periodic cell is given by the set of equations (A29)–(A37). The detailed calculus is carried out in Appendix A (Section A-2).

Model 4: vapor mass transfer model by diffusion-distillation effects

Another case of interest is given by the following situation where the dimensionless numbers are $A_l^{v} = O(\varepsilon^2)$, $P_{el}^{v} = O(\varepsilon^2)$, $N_{pl} = O(\varepsilon^2)$ and $N_{L,l} = O(1)$. The normalized forms of equations (5), (10), (12), (13), (15) and (16) are in the form

$$\varepsilon^{2} \rho_{g} \frac{\partial \omega_{v}}{\partial t} + \varepsilon^{2} \rho_{g} v_{gi} \frac{\partial \omega_{v}}{\partial y_{i}} - \frac{\partial}{\partial y_{i}} \left(\rho_{g} D \frac{\partial \omega_{v}}{\partial y_{i}} \right) = 0 \quad \text{in } \Omega_{g}$$
(68)

$$\rho_{\rm g} = \frac{M_{\rm g} P_{\rm g} |\Omega_{\rm g}|}{RT_{\rm g}} \quad \text{in } \Omega_{\rm g}. \tag{69}$$

The boundary conditions are written :

$$\varepsilon^2 \rho_a v_{pi} N_i^g + \rho_g D \frac{\partial \omega_v}{\partial y_i} N_i^g = 0 \quad \text{on } \Gamma_{gl}$$
 (70)

$$\rho_{\rm l}(\varepsilon v_{\rm li} - w_i) N_i^{\rm g} = \varepsilon^3 \rho_{\rm g}(\varepsilon^{-3} v_{\rm pi} - w_i) N_i^{\rm g} \quad \text{on } \Gamma_{\rm gl}$$
(71)

(72)

$$-\varepsilon\lambda_{g}\frac{\partial T_{g}}{\partial y_{i}}N_{i}^{g}+\lambda_{1}\frac{\partial T_{1}}{\partial y_{i}}N_{i}^{g}-\rho_{g}DL_{v}\frac{\partial\omega_{v}}{\partial y_{i}}N_{i}^{g}=0 \quad \text{on } \Gamma_{g1}$$

$$\rho_{\rm g} D \frac{\partial \omega_{\rm v}}{\partial y_i} N_i^{\rm g} = 0 \quad \text{on } \Gamma_{\rm gs}. \tag{73}$$

The homogenization process yields to the following first order macroscopic description

$$n_{g}\rho_{g}^{0}\frac{\partial\omega_{v}^{0}}{\partial t} - \frac{\partial}{\partial x_{i}}\left(D_{ij}^{*}\rho_{g}^{0}\frac{\partial\omega_{v}^{0}}{\partial x_{j}}\right) + \rho_{a}^{0}q_{v\Gamma_{gl}} = 0 \quad (74)$$

where D_{ij}^* and $q_{v\Gamma_{gl}}$ have been already defined in (52) and (53).

Note that the above model is similar to the model of Moyne *et al.* [26] [see equation (3b)].

3.2. The heat transfer model

This section is devoted to the resolution of the heat problem. The above four different situations yield different macroscopic heat transfer descriptions. Let us first investigate the heat transfer model corresponding to Models 1 and 4: $N_{pl} = O(\varepsilon^2)$ and $N_{L,l} = O(1)$. The local normalized equations are written in the form

$$\varepsilon^{2}(\rho c_{p})_{s}\frac{\partial T_{s}}{\partial t}-\frac{\partial}{\partial y_{i}}\left(\lambda_{s}\frac{\partial T_{s}}{\partial y_{i}}\right)=0 \quad \text{in } \Omega_{s}$$
(75)

$$\varepsilon^{2}(\rho c_{p})_{1}\frac{\partial T_{1}}{\partial t}+\varepsilon(\rho c_{p})_{1}v_{1i}\frac{\partial T_{1}}{\partial y_{i}}-\frac{\partial}{\partial y_{i}}\left(\lambda_{1}\frac{\partial T_{1}}{\partial y_{i}}\right)=0 \quad \text{in } \Omega_{1}$$

$$\varepsilon^{2}(\rho c_{p})_{g}\frac{\partial T_{g}}{\partial t} + \varepsilon(\rho c_{p})_{g}v_{gi}\frac{\partial T_{g}}{\partial y_{i}} - \frac{\partial}{\partial y_{i}}\left(\lambda_{g}\frac{\partial T_{g}}{\partial y_{i}}\right) = 0$$

n
$$\Omega_{\rm g}$$
. (77)

i

The above system of equations is completed by boundary conditions :

$$T_{\rm g} = T_{\rm l} \quad \text{on } \Gamma_{\rm gl} \tag{78}$$

$$-\varepsilon\lambda_{\rm g}\frac{\partial T_{\rm g}}{\partial y_i}N_i^{\rm g}+\lambda_{\rm l}\frac{\partial T_{\rm l}}{\partial y_i}N_i^{\rm g}-\rho_{\rm g}DL_{\rm v}\frac{\partial\omega_{\rm v}}{\partial y_i}N_i^{\rm g}=0\quad {\rm on}\;\Gamma_{\rm gl}$$

(79)

$$T_{\rm g} = T_{\rm s} \quad {\rm on} \ \Gamma_{\rm gs}$$
 (80)

$$\varepsilon \lambda_{\rm g} \frac{\partial T_{\rm g}}{\partial y_i} N_i^{\rm g} - \lambda_{\rm s} \frac{\partial T_{\rm s}}{\partial y_i} N_i^{\rm g} = 0 \quad \text{on } \Gamma_{\rm gs}$$
(81)

and

$$T_{\rm l} = T_{\rm s} \quad \text{on } \Gamma_{\rm ls} \tag{82}$$

$$\lambda_{\rm l} \frac{\partial T_{\rm l}}{\partial y_i} N_i^{\rm l} - \lambda_{\rm s} \frac{\partial T_{\rm s}}{\partial y_i} N_i^{\rm l} = 0 \quad \text{on } \Gamma_{\rm ls}.$$
(83)

Introducing the developments (37)-(41) in the set (75)-(83), we obtain successive boundary-value problems for the different terms of the expansions. The problems are investigated in Appendix B and yield to the macroscopic equivalent description (B41)

$$\begin{aligned} &\left[n_{\rm s}(\rho c_{\rm p})_{\rm s} + n_{\rm l}(\rho c_{\rm p})_{\rm l} \right] \frac{\partial T^0}{\partial t} - \frac{\partial}{\partial x_i} \left[\left(\lambda_{\rm sij}^* + \lambda_{\rm lij}^* \right) \frac{\partial T^0}{\partial x_j} \right] \\ &+ (\rho c_{\rm p})_{\rm l} v_{\rm lii}^{0\rm eff} \frac{\partial T^0}{\partial x_j} - L_{\rm v} \rho_{\rm a}^0 q_{\rm v \Gamma_{gi}} = 0. \end{aligned} \tag{B41}$$

The different effective coefficients in (B41) are as follows:

- $n_{\delta}, \delta = \{s, l\}$, is the volume fraction of the solid and the liquid phase
- the tensor $\lambda_{\delta ij}^*$, $\delta = \{s, l\}$, is the macroscopic (or effective) conductivity tensor of the phase δ :

$$\lambda_{\delta ij}^{*} = \frac{1}{|\Omega|} \int_{\Omega\delta} \lambda_{\delta} \left(\frac{\partial \chi_{\delta j}}{\partial y_{i}} + I_{ij} \right) \mathrm{d}\Omega. \tag{B42}$$

Note, that the above macroscopic model (B41) reveals a coupling between heat and mass transfers, as well as the models of Philip and de Vries [15, 17, 27] [from equations (1a) and (1b)] and Moyne et al. [26] [see equation (3b)]. The heat transfer is by conduction and convection incorporating a heat flux by evaporation/ condensation at the gas-liquid interface. However, it differs from Philip and de Vries model's due to the fact that the macroscopic equations (1a) and (1b) describing the combined heat and moisture transfer are derived from two independent variables: the temperature and the volumetric liquid content of the porous medium. The model (B41) has to be completed by the Darcy laws that gives the velocities v_{li} and v_{gi} in the liquid and the gas phase and the associated balance equations (Auriault [2]).

On the other hand it is possible to show that heat transfer Model related to Model 2 is (B41) where the last term becomes predominant, that yields $\rho_a^0 = 0$. However, ρ_a^0 is a dimensionless quantity that should be O(1). Therefore the heat transfer is not homogenizable. Finally the heat transfer model related to Model 3 is (B41) with a negligible phase change term.

4. CONCLUSION

The main purpose of the present paper is to produce new formulations bearing direct relevance to heat and mass transfer in liquid–gas porous solid systems. The simultaneous processes of heat and mass transfer are investigated in function of the relative weight of different dominating phenomena in presence. The problem is revisited from a theoretical point of view using a homogenization technique based on the double scale expansions. The present method allows to specify the domains where the different descriptions can be used. The heat transfer occurs by conduction and convection in presence of phase change by evaporation/ condensation.

Concerning the mass transfer, four regimes can be distinguished:

O(ε⁻²)

O(e⁻¹)

 $O(\epsilon^0)$

Ο(ε¹) 0

 $O(\epsilon^2)$

O(ε³)

O(ε⁴)

Ļ

O(ε²)

O(£3)

O(ε⁴)

↓

 $O(\epsilon^4)$

O(e³)

O : homogenizable

Fig. 2. The homogenizable and non-homogenizable domains for the mass transfer, $N_{\rm pl} \leq O(\epsilon^2)$.

Model 1:

$$n_{g}\rho_{g}^{0}\frac{\partial\omega_{v}^{0}}{\partial t} + \rho_{g}^{0}v_{gi}^{0\text{eff}}\frac{\partial\omega_{v}^{0}}{\partial x_{j}} - \frac{\partial}{\partial x_{i}}\left(D_{ij}^{*}\rho_{g}^{0}\frac{\partial\omega_{v}^{0}}{\partial x_{j}}\right) + \rho_{a}^{0}q_{v\Gamma_{v}} = 0.$$

Model 2:

$$n_{\rm g}\rho_{\rm g}^0\frac{\partial\omega_{\rm v}^0}{\partial t}+\rho_{\rm a}^0q_{\rm v\Gamma_{\rm gl}}=0.$$

Model 3:

$$n_{g}\rho_{g}^{0}\frac{\partial\omega_{v}^{0}}{\partial t}+\rho_{g}^{0}v_{gi}^{0\text{eff}}\frac{\partial\omega_{v}^{0}}{\partial x_{i}}=0.$$

Model 4:

$$n_{g}\rho_{g}^{0}\frac{\partial\omega_{v}^{0}}{\partial t}-\frac{\partial}{\partial x_{i}}\left(D_{ij}^{*}\rho_{g}^{0}\frac{\partial\omega_{v}^{0}}{\partial x_{j}}\right)+\rho_{a}^{0}q_{v\Gamma_{gi}}=0.$$

Concerning the heat transfer, Models 1 and 4 yield the same macroscopic behaviour which is written as follows:

$$(n_{\rm s}(\rho c_{\rm p})_{\rm s} + n_{\rm l}(\rho c_{\rm p})_{\rm l}) \frac{\partial T^0}{\partial t} - \frac{\partial}{\partial x_i} \left[(\lambda_{\rm sij}^* + \lambda_{\rm lij}^*) \frac{\partial T^0}{\partial x_j} \right] + (\rho c_{\rm p})_{\rm l} v_{\rm li}^{\rm 0eff} \frac{\partial T^0}{\partial x_j} - L_{\rm v} \rho_{\rm a}^0 q_{\rm v \Gamma_{gl}} = 0.$$

Model 2 shows a non homogenizable heat transfer description whereas Model 3 yields the above heat transfer relation, but with negligible phase change.

It can be shown that there are continuous passages from mass transfer Model 1 to Models 2, 3 and 4. Model 1 corresponds to the most general regime. The transient term plays a key role in the process. The



 $O(\epsilon^2)$

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0

 $O(\epsilon^1)$ O(ε⁰)

0

 $O(\epsilon^3)$

: homogenizable

 $O(\epsilon^4)$

 \cap

0

0

Ø

Per l

O(e⁻²)

Ο

0

0

0

0

C : non-homogenizable

 $O(\epsilon^{-1})$

Ø

O(e⁻¹)

 $\mathbf{P}_{el}^{\mathsf{v}}$

O(e-2)

strong vapor source at the liquid-gas interface has to be notice in Model 2, i.e., when the transient term is increased by one order of magnitude relative to Model 1. Note that in Model 4 the convection is negligible in the mass balance. Indeed, evaporation/condensation is still predominant at the upscaled macroscopic, together with diffusion.

the most general situation where convection, conduction and transport by evaporated water take place. Note also that the resulting macroscopic equation reveals a cross-coupling effect between heat and mass transfers.



 $O(\epsilon^2)$

 $O(\epsilon^1)$ O(ε⁰)







for

the

heat

T 0 Ο Ο Ο Ο 0 Ο Ο $O(\epsilon^0)$ $O(\epsilon^3)$ $O(\epsilon^2)$ $O(\epsilon^{-1})$ O(e⁻²) O(e-3) $O(\epsilon^1)$ ← O : homogenizable non-homogenizable Fig. 5. The homogenizable and non-homogenizable domains for and

 $O(\epsilon^{-3})$

O(E-2)

O(ε⁰) Ο

 $O(\epsilon^1)$ \cap

O(ε²) Ο

O(£³) 0

the heat transfer, $B_i^s = B_i^1 = B_i^s \leq O(\varepsilon)$ $P_l^{\rm l}=P_l^{\rm g}\leqslant O(1).$

In applications, e.g., geothermal engineering, all these models are of interest. In the near well regions where high pressure gradient occurs, convection is predominant. Models 1, 3 are to be used. Away from the well, convection and diffusion may become of the same order of magnitude. Model 1 is then more appropriate. Models 2 and 4 are more convenient in the regions where the liquid phase is boiling and diffuses in the air filled pores. Finally, it is necessary to use model 1 when convection, diffusion and evaporation-condensation effects become of the same order of magnitude.

The present approach allows the examination of a whole class of transport processes in heterogeneous media with respect to dominating phenomena. The necessary and very important condition for this theory to be applied is the existence of a scale separation characterizing the heterogeneity of the medium. If this requirement is not fulfilled, an equivalent macroscopic description does not exist, and the phenomenon and the medium are not homogenizable. Concerning the mass transfer, the situations called homogenizable and non-homogenizable situations for the mass transfer are shown in Figs. 2-4, and in Figs. 5 and 6 for the heat transfer, respectively.

Our investigations open up future prospects. The first application concerns for example geothermal reservoir engineering such as the exploration of the heat of hot and dry rocks. In particular, for petroleum and geothermal reservoirs, this method brings together new formulations associated with reservoirs which govern fluid dynamics and the different exchanges of matter and energy in the porous medium. Moreover, in order to obtain reliable prediction, it will be of special interest to extend the present analysis to natural fractured media. Such study should take into account the combined effects of various phenomena as the swelling of the porous matrix, the influence of hysteresis and the physicochemical interaction

 $P_I^1 = P_I^g = O(\varepsilon).$

transfer, $B_1^s = B_1^1 = B_2^s = O(\varepsilon)$

Finally, it must be stressed that the homogenization method allows to model mathematically the process of heat and mass transfer and can be applied no matter if the medium is periodic or random (Auriault [4]).

between the solid phase and the different fluids.

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A-1: Model 1—homogenization

We introduce in equations (45)–(50) asymptotic expansions in the form (37)–(41). Due to relation (42) the gradient operator $\partial/\partial y$ is changed to

APPENDIX A

$$\left(\frac{\partial}{\partial \mathbf{y}} + \varepsilon \frac{\partial}{\partial \mathbf{x}}\right). \tag{A1}$$

At the first order of approximation (46) yields

$$\rho_{\rm g}^{\rm 0} = \frac{M_{\rm g} P_{\rm g}^{\rm 0} |\Omega_{\rm g}|}{R T_{\rm g}^{\rm 0}}.$$
 (A2)

As we shall see below [see Appendix B, equation (B11)] the first order of approximation of the temperature is yindependent. From equation (43), the first approximation of the gas pressure is y-independent. Therefore (A2) gives

$$\rho_{g}^{0} = \rho_{g}^{0}(\mathbf{x}, t). \tag{A3}$$

By identifying like powers of ε , we extract from (45), (47) and (50) the following boundary value problem for ω_v^0 :

$$-\frac{\partial}{\partial y_i} \left(\rho_g^0 D \frac{\partial \omega_v^0}{\partial y_i} \right) = 0 \quad \text{in } \Omega_g \tag{A4}$$

$$\rho_{g}^{0}D\frac{\partial\omega_{v}^{0}}{\partial y_{i}}N_{i}^{g}=0 \quad \text{on } \Gamma_{gi}$$
(A5)

$$\rho_{g}^{0}D\frac{\partial\omega_{v}^{0}}{\partial y_{i}}N_{i}^{g}=0 \quad \text{on } \Gamma_{gs}$$
(A6)

where ω_v^0 is Ω -periodic.

It is possible to show that ω_v^0 does not depend on the space variable y

$$\omega_{\rm v}^0 = \omega_{\rm v}^0(\mathbf{x}, t). \tag{A7}$$

Consequently, (A2) and (A7) give

$$\rho_{a}^{0} = \rho_{g}^{0} - \rho_{v}^{0} = \rho_{a}^{0}(\mathbf{x}, t).$$
 (A8)

At the next order, taking into account the preceding relations (A3) and (A7) the cell problem for ω_v^1 becomes

$$\frac{\partial}{\partial y_i} \left[D\left(\frac{\partial \omega_i^1}{\partial y_i} + \frac{\partial \omega_v^0}{\partial x_i} \right) \right] = 0 \quad \text{in } \Omega_g \tag{A9}$$

$$D\left(\frac{\partial \omega_{v}^{l}}{\partial y_{i}} + \frac{\partial \omega_{v}^{0}}{\partial x_{i}}\right) N_{i}^{g} = 0 \quad \text{on } \Gamma_{gl}$$
(A10)

$$D\left(\frac{\partial \omega_{\mathbf{v}}^{1}}{\partial y_{i}} + \frac{\partial \omega_{\mathbf{v}}^{0}}{\partial x_{i}}\right) N_{i}^{g} = 0 \quad \text{on } \Gamma_{gs}$$
(A11)

where ω_v^1 is Ω -periodic.

It can be seen that ω_v^1 is a linear function of the the macroscopic gradient of ω_v^0

$$\omega_{\mathbf{v}}^{1} = \xi_{i} \frac{\partial \omega_{\mathbf{v}}^{0}}{\partial x_{i}} + \bar{\omega}_{\mathbf{v}}^{1}(\mathbf{x}, t).$$
 (A12)

At this stage of the process $\bar{\omega}_v^1(\mathbf{x}, t)$ is an arbitrary function of the variables \mathbf{x} and t only. Introducing the expression (A12) into equations (A9)–(A11), gives the local linear boundary value problem for ξ_i :

$$-\frac{\partial}{\partial y_i} \left[D\rho_g^0 \left(\frac{\partial \xi_j}{\partial y_i} + I_{ij} \right) \right] = 0 \quad \text{in } \Omega_g \qquad (A13)$$

$$\left[D\rho_{g}^{0}\left(\frac{\partial\xi_{j}}{\partial y_{i}}+I_{ij}\right)\right]N_{i}^{g}=0 \quad \text{on } \Gamma_{gi} \quad \text{and} \quad \Gamma_{gs} \quad (A14)$$

 ξ_i is Ω -periodic. To render the solution unique it can be chosen of zero mean value, $\langle \xi \rangle = (1/|\Omega|) \int_{\Omega_i} \xi \, d\Omega = 0$.

Let us examine the following order of approximation. The equations that govern the vapor mass fraction ω_v^2 are found to be

$$\rho_{g}^{0} \frac{\partial \omega_{v}^{0}}{\partial t} + \rho_{g}^{0} b_{gi}^{0} \left(\frac{\partial \omega_{v}^{1}}{\partial y_{i}} + \frac{\partial \omega_{v}^{0}}{\partial x_{i}} \right) - \frac{\partial}{\partial x_{i}} \left[D \rho_{g}^{0} \left(\frac{\partial \omega_{v}^{1}}{\partial y_{i}} + \frac{\partial \omega_{v}^{0}}{\partial x_{i}} \right) \right] \\ - \frac{\partial}{\partial y_{i}} \left[D \rho_{g}^{0} \left(\frac{\partial \omega_{v}^{2}}{\partial y_{i}} + \frac{\partial \omega_{v}^{1}}{\partial x_{i}} \right) \right] - \frac{\partial}{\partial y_{i}} \left[D \rho_{g}^{1} \left(\frac{\partial \omega_{v}^{1}}{\partial y_{i}} + \frac{\partial \omega_{v}^{0}}{\partial x_{i}} \right) \right] = 0 \\ \text{in } \Omega_{g} \quad (A15)$$

$$\begin{bmatrix} D\rho_{g}^{0} \left(\frac{\partial \omega_{v}^{2}}{\partial y_{i}} + \frac{\partial \omega_{v}^{1}}{\partial x_{i}} \right) \end{bmatrix} N_{i}^{g} + \begin{bmatrix} D\rho_{g}^{1} \left(\frac{\partial \omega_{v}^{1}}{\partial y_{i}} + \frac{\partial \omega_{v}^{0}}{\partial x_{i}} \right) \end{bmatrix} N_{i}^{g}$$
$$= -\rho_{a}^{0} v_{pi}^{0} N_{i}^{g} \quad \text{on } \Gamma_{gi} \quad (A16)$$

$$\left[D\rho_{g}^{0} \left(\frac{\partial \omega_{i}^{v}}{\partial y_{i}} + \frac{\partial \omega_{i}^{v}}{\partial x_{i}} \right) \right] N_{j}^{g} + \left[D\rho_{g}^{1} \left(\frac{\partial \omega_{i}^{v}}{\partial y_{i}} + \frac{\partial \omega_{i}^{v}}{\partial x_{i}} \right) \right] N_{j}^{g} = 0$$
on Γ_{gs} (A17)

 ω_v^2 is Ω -periodic.

The existence of ω_v^2 introduces a compatibility condition. Equation (A15) can be seen as the balance of the periodic flux

$$-D\rho_{g.}^{0}\left(\frac{\partial\omega_{v}^{2}}{\partial y_{i}}+\frac{\partial\omega_{v}^{1}}{\partial x_{i}}\right)-D\rho_{g}^{1}\left(\frac{\partial\omega_{v}^{1}}{\partial y_{i}}+\frac{\partial\omega_{v}^{0}}{\partial x_{i}}\right)$$

in the presence of the source

$$\rho_{g}^{0}\frac{\partial\omega_{v}^{0}}{\partial t}+\rho_{g}^{0}v_{gi}^{0}\left(\frac{\partial\omega_{v}^{1}}{\partial y_{i}}+\frac{\partial\omega_{v}^{0}}{\partial x_{i}}\right)-\frac{\partial}{\partial x_{i}}\left[D\rho_{g}^{0}\left(\frac{\partial\omega_{v}^{1}}{\partial y_{i}}+\frac{\partial\omega_{v}^{0}}{\partial x_{i}}\right)\right].$$

The periodicity of the flux imposes condition on the sources. This can easily be checked by integration (A15) over Ω_{g} . Using the divergence theorem, the periodicity property and the conditions (A16) and (A17) on the boundaries Γ_{gl} and Γ_{gs} , yields

$$\rho_{g}^{0} \frac{\partial \omega_{v}^{0}}{\partial t} \int_{\Omega_{g}} d\Omega + \rho_{g}^{0} \int_{\Omega_{g}} v_{gi}^{0} \left(\frac{\partial \omega_{v}^{1}}{\partial y_{i}} + \frac{\partial \omega_{v}^{1}}{\partial x_{i}} \right) d\Omega - \frac{\partial}{\partial x_{i}} \rho_{g}^{0}$$
$$\times \int_{\Omega_{g}} D \left(\frac{\partial \omega_{v}^{1}}{\partial y_{i}} + \frac{\partial \omega_{v}^{0}}{\partial x_{i}} \right) d\Omega + \rho_{a}^{0} \int_{\Gamma_{gi}} v_{pi}^{0} N_{i}^{g} d\mathbf{S} = 0. \quad (A18)$$

Introducing now the relations (A12) for ω_v^1 , (A16) and (A17) for the gas velocity, and dividing by $|\Omega|$ gives the first order macroscopic description

$$n_{g}\rho_{g}^{0}\frac{\partial\omega_{v}^{0}}{\partial t}+\rho_{g}^{0}v_{gi}^{0}\frac{\partial\omega_{v}^{0}}{\partial x_{j}}-\frac{\partial}{\partial x_{i}}\left(D_{ij}^{*}\rho_{g}^{0}\frac{\partial\omega_{v}^{0}}{\partial x_{j}}\right)+\rho_{a}^{0}q_{v\Gamma_{gi}}=0.$$
(A19)

The different effective parameters in the equation (A19) are as follows:

• the porosity of the gaseous phase

$$n_{\rm g} = \frac{|\Omega_{\rm g}|}{|\Omega|} \tag{A20}$$

• the tensor D_{ij}^* is the macroscopic (or effective) diffusion tensor:

$$D_{ij}^{*} = \frac{1}{|\Omega|} \int_{\Omega_{s}} D\left(\frac{\partial \xi_{j}}{\partial y_{i}} + I_{ij}\right) d\Omega$$
 (A21)

• $q_{v\Gamma_g}$ is the vapor source per unit volume defined as the volume average

$$q_{\mathbf{v}\Gamma_{gi}} = \frac{1}{|\Omega|} \int_{\Omega_{gi}} v_{pi}^0 N_i^g \, \mathrm{d}\mathbf{S}. \tag{A22}$$

Elsewhere, the first order approximation of equation (48) yields

$$\rho_{g}^{0} v_{pi}^{0} N_{i}^{g} = -\rho_{i} w_{i}^{0} N_{i}^{g}. \tag{A23}$$

By integrating on Γ_{gl} it becomes

$$\int_{\Gamma_{gl}} \rho_g^0 v_{pl}^0 N_l^g \, \mathrm{d}\mathbf{S} = -\int_{\Gamma_{gl}} \rho_l w_l^0 N_l^g \, \mathrm{d}\mathbf{S}$$
$$= -\rho_l \frac{\mathrm{d}}{\mathrm{d}t} \left(\int_{\Omega_l} \mathrm{d}\Omega \right) = -\rho_l \frac{\mathrm{d}|\Omega_l|}{\mathrm{d}t}. \quad (A24)$$

Then we get

$$q_{v\Gamma_{g}} = \frac{1}{|\Omega|} \int_{\Gamma_{g}} v_{pl}^{0} N_{l}^{g} dS = -\frac{\rho_{l}}{\rho_{g}^{0}} \frac{d}{dt} \left(\frac{|\Omega_{l}|}{|\Omega|}\right) = -\frac{\rho_{l}}{\rho_{g}^{0}} \frac{d}{dt} (n_{l})$$
(A25)

where $n_{\rm l} = |\Omega_{\rm l}|/|\Omega|$ is the water volume fraction.

On the other hand, from (A2), the porosity of the gaseous phase is written

$$n_{g} = \frac{|\Omega_{g}|}{|\Omega|} = \frac{1}{|\Omega|} \frac{R}{M_{g}} \frac{\rho_{g}^{0} T_{g}^{0}}{P_{g}^{0}}.$$
 (A26)

Elsewhere

$$n_{\rm g} = 1 - (n_{\rm i} + n_{\rm s})$$
 (A27)

then, due to relations (A25)–(A27), the vapor source becomes

$$q_{\mathbf{v}\Gamma_{g}} = \frac{1}{|\Omega|} \frac{\rho_{\mathrm{l}}}{\rho_{\mathrm{g}}^{0}} \frac{R}{M_{\mathrm{g}}} \frac{\mathrm{d}}{\mathrm{d}t} \left(\frac{\rho_{\mathrm{g}}^{0} T_{\mathrm{g}}^{0}}{P_{\mathrm{g}}^{0}} \right). \tag{A28}$$

A-2: Model 3—determination of the vector field ξ : The boundary value problem for ω_v^1 is written

$$\rho_{g}^{0} \frac{\partial \omega_{v}^{0}}{\partial t} + \rho_{g}^{0} v_{gi}^{0} \left(\frac{\partial \omega_{v}^{1}}{\partial y_{i}} + \frac{\partial \omega_{v}^{0}}{\partial x_{i}} \right) - \frac{\partial}{\partial y_{i}} \left[D \rho_{g}^{0} \left(\frac{\partial \omega_{v}^{1}}{\partial y_{i}} + \frac{\partial \omega_{v}^{0}}{\partial x_{i}} \right) \right] = 0$$

in Ω_{g} (A29)

$$D\left(\frac{\partial \omega_{\rm v}^{\rm l}}{\partial y_i} + \frac{\partial \omega_{\rm v}^{\rm 0}}{\partial x_i}\right) N_i^{\rm g} = 0 \quad \text{on } \Gamma_{\rm gl} \tag{A30}$$

$$D\left(\frac{\partial \omega_{v}^{1}}{\partial y_{i}}+\frac{\partial \omega_{v}^{0}}{\partial x_{i}}\right)N_{i}^{g}=0 \quad \text{on } \Gamma_{gs}.$$
(A31)

In that case ξ_i is not only y-dependent but it also depends on the macroscopic gradient of pressure of the gas phase $\nabla_x p_g^0$

$$\omega_{\mathbf{v}}^{1} = \xi_{i} \frac{\partial \omega_{\mathbf{v}}^{1}}{\partial x_{i}} + \bar{\omega}_{\mathbf{v}}^{1}(\mathbf{x}, t)$$
 (A32)

where

$$\xi_i = \xi_i (\nabla_{\mathbf{x}} P_g^0, \mathbf{y}) \text{ is y-periodic.}$$
(A33)

The vector field is in this case the solution of the following cell problem:

$$-\rho_{g}^{0}v_{gi}^{0}+\rho_{g}^{0}v_{gi}^{0}\left(\frac{\partial\xi_{i}}{\partial y_{j}}+I_{ij}\right)-\frac{\partial}{\partial y_{j}}\left(\rho_{g}^{0}D\left(\frac{\partial\xi_{i}}{\partial y_{j}}+I_{ij}\right)\right)=0$$

$$\rho_g^0 D\left(\frac{\partial \xi_i}{\partial y_j} + I_{ij}\right) N_i^g = 0 \quad \text{on} \quad \Gamma_{gl} \quad \text{and} \quad \Gamma_{gs} \quad (A35)$$

where

$$\langle \xi \rangle = \frac{1}{|\Omega|} \int_{\Omega_s} \xi \, \mathrm{d}\Omega = 0.$$
 (A36)

APPENDIX B: THE HEAT TRANSFER MODEL-HOMOGENIZATION

Recall that all the quantities appearing in equations (75)-(77), (79), (81) and (83) are dimensionless and the terms in factor of ε^2 , ε and ε^0 are of order 1.

At the first order we have

$$-\frac{\partial}{\partial y_i} \left(\lambda_{\rm s} \frac{\partial T_{\rm s}^0}{\partial y_i} \right) = 0 \quad \text{in } \Omega_{\rm s}$$
 (B1)

$$-\frac{\partial}{\partial y_i} \left(\lambda_1 \frac{\partial T_1^0}{\partial y_i} \right) = 0 \quad \text{in } \Omega_1$$
 (B2)

$$-\frac{\partial}{\partial y_i} \left(\lambda_{g} \frac{\partial T_{g}^{0}}{\partial y_i} \right) = 0 \quad \text{in } \Omega_{g}.$$
 (B3)

The boundary conditions are:

$$T_1^0 = T_g^0 \quad \text{on } \Gamma_{gl} \tag{B4}$$

$$\lambda_{l} \frac{\partial T_{1}^{0}}{\partial y_{i}} N_{i}^{g} = 0 \quad \text{on } \Gamma_{gl}$$
(B5)

$$T_s^0 = T_g^0 \quad \text{on } \Gamma_{gs} \tag{B6}$$

$$\lambda_{\rm s} \frac{\partial T_{\rm s}^0}{\partial y_i} N_i^{\rm g} = 0 \quad \text{on } \Gamma_{\rm gs} \tag{B7}$$

$$T_1^0 = T_s^0 \quad \text{on } \Gamma_{ls} \tag{B8}$$

$$\lambda_{i} \frac{\partial T_{1}^{0}}{\partial y_{i}} N_{i}^{i} - \lambda_{s} \frac{\partial T_{s}^{0}}{\partial y_{i}} N_{i}^{i} = 0 \quad \text{on } \Gamma_{is}.$$
 (B9)

From equations (B1), (B2), (B5), (B7)-(B9) comes:

$$T_1^0 = T_s^0 = T^0(\mathbf{x}, t).$$
 (B10)

Taking now into account equation (B3), (B4) and (B6) yields :

$$T_{\mathbf{g}}^{0} = T_{1}^{0} = T_{s}^{0} = T^{0}(\mathbf{x}, t).$$
 (B11)

By using the above relation, it comes at the second order of approximation

$$-\frac{\partial}{\partial y_i} \left[\lambda_s \left(\frac{\partial T_s^1}{\partial y_i} + \frac{\partial T^0}{\partial x_i} \right) \right] = 0 \quad \text{in } \Omega_s$$
 (B12)

$$-\frac{\partial}{\partial y_i} \left[\lambda_1 \left(\frac{\partial T_1^1}{\partial y_i} + \frac{\partial T^0}{\partial x_i} \right) \right] = 0 \quad \text{in } \Omega_1 \tag{B13}$$

$$-\frac{\partial}{\partial y_i} \left[\lambda_{g} \left(\frac{\partial T_{g}^{1}}{\partial y_i} + \frac{\partial T^{0}}{\partial x_i} \right) \right] = 0 \quad \text{in } \Omega_{g}$$
(B14)

$$T_{i}^{1} = T_{g}^{1} \quad \text{on } \Gamma_{gi} \tag{B15}$$

$$\lambda_t \left(\frac{\partial T_1^1}{\partial y_i} + \frac{\partial T^0}{\partial x_i} \right) N_i^g = 0 \quad \text{on } \Gamma_{gl}$$
(B16)

in Ω_g (A34) where (A10) has been taken into account.

$$T_{\rm s}^{\rm l} = T_{\rm g}^{\rm l} \quad \text{on } \Gamma_{\rm gs} \tag{B17}$$

$$\lambda_{\rm s} \left(\frac{\partial T_{\rm s}^1}{\partial y_i} + \frac{\partial T^0}{\partial x_i} \right) N_i^{\rm g} = 0 \quad \text{on } \Gamma_{\rm gs} \tag{B18}$$

$$T_1^1 = T_s^1 \quad \text{on } \Gamma_{1s} \tag{B19}$$

$$\lambda_{s} \left(\frac{\partial T_{s}^{1}}{\partial y_{i}} + \frac{\partial T^{0}}{\partial x_{i}} \right) N_{i}^{1} - \lambda_{i} \left(\frac{\partial T_{1}^{1}}{\partial y_{i}} + \frac{\partial T^{0}}{\partial x_{i}} \right) N_{i}^{1} = 0 \quad \text{on } \Gamma_{1s}.$$
(B20)

It can be shown that the periodic field temperature T^1_{α} is a linear function of the macroscopic gradient of T^0 , up to an arbitrary function $\overline{T}_{\alpha}^{1}$:

$$T_{\alpha}^{I} = \chi_{\alpha i} \frac{\partial T^{0}}{\partial x_{i}} + \bar{T}_{\alpha}^{I}(\mathbf{x}, t)$$
 (B21)

where $\alpha = \{s, l, g\}$ is for the solid, the liquid and the gas phase, respectively.

The functions $\chi_{\alpha i}$ are given by the following boundary value problem :

$$\frac{\partial}{\partial y_i} \left[\lambda_{\alpha} \left(\frac{\partial \chi_{\alpha j}}{\partial y_i} + I_{ij} \right) \right] = 0 \quad \text{in } \Omega_{\alpha}$$
(B22)

$$\lambda_{\delta} \left(\frac{\partial \chi_{\delta j}}{\partial y_i} + I_{ij} \right) N_i^g = 0 \quad \text{on } \Gamma_{g\delta}$$
(B23)

$$\lambda_{\rm s} \left(\frac{\partial \chi_{sj}}{\partial y_i} + I_{ij} \right) N_i^{\rm l} = \lambda_{\rm l} \left(\frac{\partial \chi_{lj}}{\partial y_i} + I_{ij} \right) \quad \text{on } \Gamma_{\rm ls} \qquad (B24)$$

$$\chi_{gj} = \chi_{lj} = \chi_{sj} \tag{B25}$$

$$\langle \chi_{\alpha j} \rangle = 0$$
 (B26)

where $\alpha = \{s, l, g\}$ and $\delta = \{s, l\}$. $\chi_{\alpha i}$ is Ω -periodic. At the third order, the homogenization process gives :

$$(\rho c_{p})_{s} \frac{\partial T^{0}}{\partial t} - \frac{\partial}{\partial y_{i}} \left[\lambda_{s} \left(\frac{\partial T_{s}^{1}}{\partial y_{i}} + \frac{\partial T_{s}^{1}}{\partial x_{i}} \right) \right] - \frac{\partial}{\partial x_{i}} \left[\lambda_{s} \left(\frac{\partial T_{s}^{1}}{\partial y_{i}} + \frac{\partial T^{0}}{\partial x_{i}} \right) \right] = 0 \quad \text{in } \Omega_{s} \quad (B27)$$

$$(\rho c_{p})_{l} \frac{\partial T^{0}}{\partial t} - \frac{\partial}{\partial y_{i}} \left[\lambda_{l} \left(\frac{\partial T_{l}^{2}}{\partial y_{i}} + \frac{\partial T_{l}^{1}}{\partial x_{i}} \right) \right] - \frac{\partial}{\partial x_{i}} \left[\lambda_{l} \left(\frac{\partial T_{l}^{1}}{\partial y_{i}} + \frac{\partial T^{0}}{\partial x_{i}} \right) \right] + (\rho c_{p})_{l} v_{l'}^{0} \left(\frac{\partial T_{l}^{1}}{\partial y_{i}} + \frac{\partial T^{0}}{\partial x_{i}} \right) = 0 \quad \text{in } \Omega_{l} \quad (B28)$$

$$\rho_{g}^{0}c_{pg}\frac{\partial T^{0}}{\partial t} - \frac{\partial}{\partial y_{i}}\left[\lambda_{g}\left(\frac{\partial T_{g}^{2}}{\partial y_{i}} + \frac{\partial T_{g}^{1}}{\partial x_{i}}\right)\right] - \frac{\partial}{\partial x_{i}}\left[\lambda_{g}\left(\frac{\partial T_{g}^{1}}{\partial y_{i}} + \frac{\partial T^{0}}{\partial x_{i}}\right)\right] + c_{pg}\rho_{g}^{0}v_{g'}^{0}\left(\frac{\partial T_{g}^{1}}{\partial y_{i}} + \frac{\partial T^{0}}{\partial x_{i}}\right) = 0 \quad \text{in } \Omega_{g} \quad (B29)$$

$$= T_{\rm g}^2 \quad \text{on } \Gamma_{\rm gi} \tag{B30}$$

$$\lambda_{i} \left(\frac{\partial T_{i}^{2}}{\partial y_{i}} + \frac{\partial T_{i}^{1}}{\partial x_{i}} \right) N_{i}^{g} - \lambda_{g} \left(\frac{\partial T_{g}^{1}}{\partial y_{i}} + \frac{\partial T^{0}}{\partial x_{i}} \right) N_{i}^{g} \\ - \left[DL_{v} \rho_{g}^{0} \left(\frac{\partial \omega_{v}^{2}}{\partial y_{i}} + \frac{\partial \omega_{v}^{1}}{\partial x_{i}} \right) \right] N_{i}^{g}$$

 T_1^2

$$-\left[DL_{v}\rho_{g}^{1}\left(\frac{\partial\omega_{v}^{1}}{\partial y_{i}}+\frac{\partial\omega_{v}^{0}}{\partial x_{i}}\right)\right]N_{i}^{g}=0 \quad \text{on } \Gamma_{gi} \quad (B31)$$

or with (A16)

$$\lambda_1 \left(\frac{\partial T_i^2}{\partial y_i} + \frac{\partial T_i^1}{\partial x_i} \right) N_i^{\mathfrak{g}} - \lambda_{\mathfrak{g}} \left(\frac{\partial T_{\mathfrak{g}}^1}{\partial y_i} + \frac{\partial T^0}{\partial x_i} \right) N_i^{\mathfrak{g}} + L_{\mathfrak{v}} \rho_{\mathfrak{s}}^0 v_{\mathfrak{p}i}^0 N_i^{\mathfrak{g}} = 0$$

on
$$\Gamma_{gl}$$
 (B32)

$$T_{\rm s}^2 = T_{\rm g}^2 \quad \text{on } \Gamma_{\rm gs} \tag{B33}$$

$$\lambda_{s}\left(\frac{\partial T_{s}^{2}}{\partial y_{i}}+\frac{\partial T_{s}^{1}}{\partial x_{i}}\right)N_{i}^{s}-\lambda_{g}\left(\frac{\partial T_{g}^{1}}{\partial y_{i}}+\frac{\partial T^{0}}{\partial x_{i}}\right)N_{i}^{s}=0 \quad \text{on } \Gamma_{gs}$$

$$T_1^2 = T_s^2 \quad \text{on } \Gamma_{\rm is} \tag{B35}$$

$$\lambda_{s}\left(\frac{\partial T_{s}^{s}}{\partial y_{i}}+\frac{\partial T_{s}^{l}}{\partial x_{i}}\right)N_{i}^{1}-\lambda_{t}\left(\frac{\partial T_{t}^{2}}{\partial y_{i}}+\frac{\partial T_{t}^{1}}{\partial x_{i}}\right)N_{i}^{1}=0 \quad \text{on } \Gamma_{ts}.$$

(B36)

Integrating equation (B27) in Ω_s and equation (B28) in Ω_i and using the divergence theorem give successively In Ω_s :

$$\int_{\Omega_{s}} (\rho c_{p})_{s} \frac{\partial T^{0}}{\partial t} d\Omega - \int_{\Omega_{s}} \frac{\partial}{\partial y_{i}} \left[\lambda_{s} \left(\frac{\partial T_{s}^{2}}{\partial y_{i}} + \frac{\partial T_{s}^{1}}{\partial x_{i}} \right) \right] d\Omega$$
$$- \int_{\Omega_{s}} \frac{\partial}{\partial x_{i}} \left[\lambda_{s} \left(\frac{\partial T_{s}^{1}}{\partial y_{i}} + \frac{\partial T^{0}}{\partial x_{i}} \right) \right] d\Omega = 0 \quad (B37)$$

or

$$\begin{aligned} |\Omega_{s}|(\rho c_{p})_{s} \frac{\partial T^{0}}{\partial t} &- \frac{\partial}{\partial x_{i}} \frac{\partial T^{0}}{\partial x_{j}} \int_{\Omega_{s}} \lambda_{s} \left(\frac{\partial \chi_{sj}}{\partial y_{i}} + I_{ij} \right) \mathrm{d}\Omega \\ &- \int_{\Gamma_{p}} \lambda_{s} \left(\frac{\partial T_{s}^{2}}{\partial y_{i}} + \frac{\partial T_{s}^{1}}{\partial x_{i}} \right) N_{i}^{s} \mathrm{d}S \end{aligned}$$

 $-\int_{\Gamma_{b}}\lambda_{s}\left(\frac{\partial T_{s}^{2}}{\partial y_{i}}+\frac{\partial T_{s}^{1}}{\partial x_{i}}\right)N_{i}^{s}\,\mathrm{d}S=0.$ (B38)

In Ω_l :

$$\begin{split} \int_{\Omega_{i}} (\rho c_{p})_{1} \frac{\partial T^{0}}{\partial t} d\Omega &- \int_{\Omega_{i}} \frac{\partial}{\partial y_{i}} \left[\lambda_{1} \left(\frac{\partial T_{1}^{1}}{\partial y_{i}} + \frac{\partial T_{1}^{1}}{\partial x_{i}} \right) \right] d\Omega \\ &- \int_{\Omega_{i}} \frac{\partial}{\partial x_{i}} x \left[\lambda_{1} \left(\frac{\partial T_{1}^{1}}{\partial y_{i}} + \frac{\partial T^{0}}{\partial x_{i}} \right) \right] d\Omega \\ &+ \int_{\Omega_{i}} (\rho c_{p})_{i} v_{ii}^{0} \left(\frac{\partial T_{i}^{1}}{\partial y_{i}} + \frac{\partial T^{0}}{\partial x_{i}} \right) d\Omega = 0 \quad (B39) \end{split}$$

or

$$\begin{split} |\Omega_{\mathbf{i}}|(\rho c_{\mathbf{p}})_{\mathbf{i}} \frac{\partial T^{0}}{\partial t} &- \frac{\partial}{\partial x_{i}} \frac{\partial T^{0}}{\partial x_{j}} \int_{\Omega_{\mathbf{i}}} \lambda_{\mathbf{i}} \left(\frac{\partial \chi_{ij}}{\partial y_{i}} + I_{ij} \right) \mathrm{d}\Omega + (\rho c_{\mathbf{p}})_{\mathbf{i}} \frac{\partial T^{0}}{\partial x_{j}} \\ &\times \int_{\Omega_{\mathbf{i}}} \mathbf{v}_{ii}^{0} \left(\frac{\partial \chi_{ij}}{\partial y_{i}} + I_{ij} \right) \mathrm{d}\Omega - \int_{\Gamma_{\mathbf{g}}} \lambda_{\mathbf{i}} \left(\frac{\partial T_{\mathbf{i}}^{2}}{\partial y_{i}} + \frac{\partial T_{\mathbf{i}}^{1}}{\partial x_{i}} \right) N_{\mathbf{i}}^{\mathbf{i}} \mathrm{d}S \\ &- \int_{\Gamma_{\mathbf{b}}} \lambda_{\mathbf{i}} \left(\frac{\partial T_{\mathbf{i}}^{2}}{\partial y_{i}} + \frac{\partial T_{\mathbf{i}}^{1}}{\partial x_{i}} \right) N_{\mathbf{i}}^{\mathbf{i}} \mathrm{d}S = 0. \quad (\mathbf{B40}) \end{split}$$

After using the periodicity property and the conditions on the boundaries Γ_{ls} , Γ_{gs} , Γ_{gl} , integrating (B14) over Ω_g and adding member to member (B38) and (B40), we obtain the macroscopic description

$$(n_{s}(\rho c_{p})_{s} + n_{i}(\rho c_{p})_{i})\frac{\partial T^{0}}{\partial t} - \frac{\partial}{\partial x_{i}} \left[(\lambda_{sij}^{*} + \lambda_{lij}^{*})\frac{\partial T^{0}}{\partial x_{j}} \right]$$
$$+ (\rho c_{p})_{i} v_{li}^{0} \frac{\partial T^{0}}{\partial x_{j}} - L_{v} \rho_{a}^{0} q_{v\Gamma_{gl}} = 0 \quad (B41)$$

where the different effective coefficients defined are as follows:

- $n_{\delta}, \delta = \{s, l\}$, is the volume fraction of the solid and the liquid phase
- the tensor $\lambda_{\delta ij}^*, \delta=\{{\rm s},{\rm l}\},$ is the macroscopic (or effective) conductivity tensor defined as

$$\lambda_{ij}^{*} = \frac{1}{|\Omega|} \int_{\Omega_{\delta}} \lambda_{\delta} \left(\frac{\partial \chi_{\delta j}}{\partial y_{i}} + I_{ij} \right) d\Omega.$$
 (B42)