

Appendix 1. Fluid, heat and mass transport equations in porous media

1.1. *Formulation of the problem of heat and mass transfer in a porous medium (macroscopic level)*

This appendix gives a mathematical description of the problem of heat and mass transfer in a porous medium. The core of the mathematical modeling is defined by the fundamental physical principles of:

- Mass conservation of the fluid
- Mass conservation of the solute
- Conservation of the linear momentum of the fluid
- Energy conservation

In the continuum approach, mass, motion and energy-related quantities can be defined in a 'microscopic' (local) volume element for which balance laws are postulated. Mass, linear momentum and energy represent extensive properties, i.e. quantities which are additive over volumes of the continuum. On the other hand, intensive properties concern densities of these extensive properties being independent of the balance volume.

In principle, given the initial and boundary conditions, the transport problem in a porous medium can be solved at the continuum (microscopic) level. However, this approach is not feasible in practice because at that level it is not possible to describe the configuration of the surface that bounds the considered phase (i.e., the solid surface bounding the considered fluid phase filling the void space) except in simple cases such as a medium composed of straight capillary tubes. Moreover constitutive equations require coefficients that can only be determined experimentally and that obviously can't be measured at a microscopic level in real system.

In order to circumvent these difficulties, the transport problem is lifted from microscopic level to a macroscopic one, i.e. a coarser level of averaging is reached (upscaling or macroscopization). This is still a continuum approach but on a higher level at which quantities can be measured and problem boundaries can be identified. As a consequence, the real porous medium domain is regarded as a conceptual model in which each phase is assumed to behave

as a continuum filling the entire domain. At every point within these continua, values are assigned for the variables and parameters involved, and they are averaged over a Representative Elementary Volume (REV). To allow the passage from the microscopic to the macroscopic level, parameters such as porosity ϕ , tortuosity, permeability \mathbf{k} , dispersivity \mathbf{D} , etc. have to be introduced. The numerical value of these coefficients must be determined experimentally or in the field. These coefficients are related to the chosen model of the considered problem but for convention are referred to the porous medium.

At this stage, an important remark on the appropriate size of REV has to be made: since the macroscopic parameters have the meaning of average values over a REV centered in the point where the parameter is measured, the latter will be useful only if the measuring device also averages over the same REV scale. That is, a strong relationship exists between the REV size of a porous medium and the measuring instrument. Moreover, referring to fractured media, the concept of a REV can be impractical or even invalid as in the case where fractures create a non-leaching network (Georgiadis 1991).

To obtain the macroscopic balance equations, some averaging rules (closure) to the corresponding microscopic equations must be applied. The averaging method has been developed over 30 years with majors contributions from Bear and Bachmat (1990), Hassanizadeh and Gray (1979a, 1979b, 1980, 1986a, 1986b). Here the problem of heat and mass transfer in porous medium will be directly formulated as a set of average equations in the dependent average variables $C, \rho_f, p, \mu, \mathbf{V}^*, T_f, T_s$. In this context, a single-phase fluid that occupies the entire void space of a porous medium, is considered. In the equations, fluid and solid phase will be labeled with f and s subscript, respectively. Fluid is a binary system (for instance, water and a non-reactive solute which concentration is denoted by C) with molecular diffusion D_{diff} . All fluxes are expressed per unit of area.

Equation 1: Mass conservation of the fluid.

$$\boxed{\begin{aligned} \frac{\partial}{\partial t} \phi \rho_f + \text{div}(\rho_f \mathbf{q}) &= 0 \\ \mathbf{q} &= \phi \mathbf{V}^* \end{aligned}} \quad (1.1)$$

where ϕ is the porosity of the porous medium, \mathbf{q} is the Darcy (or volumetric flux density velocity) signifying the specific discharge of the fluid, \mathbf{V}^* is also often referred to as pore

velocity.

Usually the mass conservation balance is implemented in the simulations codes in a different form that can be obtained by developing the derivatives in (1.1):

$$\phi \underbrace{\frac{\partial \rho_f}{\partial t}}_{\rho_f \left(\bar{\alpha} \frac{\partial C}{\partial t} - \bar{\beta} \frac{\partial T}{\partial t} + \bar{\gamma} \frac{\partial p_f}{\partial t} \right)} + \rho_f \underbrace{\frac{\partial \phi}{\partial t}}_{(1-\phi)\Upsilon \frac{\partial p_f}{\partial t}} + \rho_f \text{div}(\mathbf{q}) + \mathbf{q} \cdot \underbrace{\mathbf{grad}(\rho_f)}_{\rho_f (\bar{\alpha} \mathbf{grad} C - \bar{\beta} \mathbf{grad} T + \bar{\gamma} \mathbf{grad} p_f)} = 0$$

Simplifications yield to:

$$S_0 \frac{\partial p_f}{\partial t} + \text{div}(\mathbf{q}) = Q_{Bous sin esq} \quad (1.2)$$

where:

$Q_{Bous sin esq} = -\mathbf{q} \cdot (\bar{\alpha} \mathbf{grad} C - \bar{\beta} \mathbf{grad} T + \bar{\gamma} \mathbf{grad} \phi) - \phi \left(\bar{\alpha} \frac{\partial C}{\partial t} - \bar{\beta} \frac{\partial T}{\partial t} \right)$ is a term resulting from the developed derivatives of (1.1) which incorporates mass-dependent and temperature dependent compression effects.

$S_0 = \phi \bar{\gamma} + (1 - \phi) \Upsilon$ is the specific storage coefficient or medium storativity which physically represents the volume of water released (or added to) from storage in the aquifer per unit volume of aquifer and per unit decline (or rise) of head, Υ being the bulk compressibility.

Equation 2: Mass conservation of the solute.

$$\frac{\partial \phi C}{\partial t} + \text{div}(\rho_f C \mathbf{q}) + \text{div}(\bar{\mathbf{j}}_c^*) - \text{div}(\mathbf{D}_{disp} \mathbf{grad}(C)) = Q^C \quad (1.3)$$

Q^C is a mass supply.

Three different kind of fluxes are involved: $C \mathbf{q}$ is an advective flux, $\bar{\mathbf{j}}_c^*$ is a diffusive flux and $\mathbf{D}_{disp} \mathbf{grad}(C)$ a dispersive flux. As a phenomenological law, dispersive flux is regarded as a diffusion-like process, hence it depends on a concentration gradient. \mathbf{D}_{disp} is the tensor of mechanical dispersion which physical meaning is explained in the next paragraph.

The advective flux represents the quantity of mass advected by the pore velocity \mathbf{V}^* per unit area of the porous medium.

$\bar{\mathbf{j}}_c^*$ expresses the flux of the solute at macroscopic level.

$$\bar{\mathbf{j}}_c^* = -\phi \bar{\mathbf{D}}_{\text{diff}} \mathbf{grad}(C) \quad (1.4)$$

Here $\bar{\mathbf{D}}_{\text{diff}}$ is a tensor and is called coefficient of molecular diffusion in a (saturated) porous medium.

By substituting (1.4) in (1.3):

$$\boxed{\frac{\partial \phi C}{\partial t} + \text{div}(\rho_f \mathbf{q} C) - \text{div}(\mathbf{D} \mathbf{grad}(C)) = Q_C} \quad (1.5)$$

where

$$\mathbf{D} = \mathbf{D}_{\text{disp}} + \phi \bar{\mathbf{D}}_{\text{diff}} \quad (1.6)$$

is the tensor of hydrodynamic dispersion. This coefficient includes the effects of both mechanical dispersion and molecular diffusion.

Hydrodynamic dispersion is a phenomena that arises whenever a solute carried by a fluid flows through a porous medium. For instance, if a uniform flow in a 2D porous medium is considered, experience shows that as flow takes place the solute gradually spreads occupying a portion of the flow domain both in the direction of the uniform flow (referred to as longitudinal) and also in its normal direction (transversal). The observed spreading (at macroscopic level) results from two inseparable processes occurring at microscopic level: the mechanical dispersion and the molecular diffusion. The two basics factor that produce mechanical dispersion are the flow itself and the presence of the pore system through which flow takes place: because of the shape of the interconnected pore space, a close group of tracer particles will spread throughout the flow domain primarily in the longitudinal direction. Essentially, dispersive flux of the mass solute expresses the rate at which mass is transported because of the velocity variations in the void space of the REV. Very little spreading in a direction transversal to the flow can be produced by velocity variations only. Therefore, an additional flux referred to as molecular diffusion takes place in the pore space. In hydrodynamic context, molecular diffusion cannot be separated from mechanical dispersion although molecular diffusion can take place alone also in absence of motion. Its effect on the overall dispersion is more significant at low velocities while at high velocities it can be negligible. A parameter that allows us to estimate which process is dominant in hydrodynamic dispersion is the Peclet number defined as

$$\text{Pe}_D = \frac{L |\mathbf{V}^*|}{\mathbf{D}_{\text{diff}}} \quad (1.7)$$

where L is a characteristic length. The Peclet number is the ratio between rate of transport by convection to the rate of transport by molecular diffusion.

If $Pe_D \ll 1$ then diffusion will control the flow otherwise if $Pe_D \gg 1$ the flow is advective-dominated

Equation 3: Conservation of linear momentum of the fluid (equation of motion).

$$\mathbf{V}^* = -\frac{\mathbf{k}}{\phi\mu_{0f}} f_\mu (\mathbf{grad}(p_f) - \rho_f \mathbf{g}) \quad (1.8)$$

where \mathbf{k} is the tensor of permeability.

Equation of motion can be rewritten in terms of the piezometric head $\varphi = z + \frac{p_f}{\rho_{0f}g}$

The differentiation of this relation yields to $\mathbf{grad}(p_f) = \rho_{0f}g (\mathbf{grad}(\varphi) - 1)$, hence:

$$\mathbf{q} = -\frac{\mathbf{k}\rho_{0f}g}{\mu_{0f}} f_\mu \mathbf{grad}(\varphi + \frac{\rho_f - \rho_{0f}}{\rho_{0f}}) = -\mathbf{K}f_\mu \mathbf{grad}(\varphi + \frac{\rho_f - \rho_{0f}}{\rho_{0f}}) \quad (1.9)$$

where

$$\mathbf{K} = \frac{\mathbf{k}\rho_{0f}g}{\mu_{0f}} \quad (1.10)$$

is the hydraulic conductivity tensor related to the reference fluid density ρ_{0f} . Eq. (1.9) is the extension of Darcy's experimental law to a 3D anisotropic media.

The term

$$f_\mu = \frac{\mu_{0f}}{\mu_f(\varphi, C, T)} \quad (1.11)$$

is the viscosity function which takes into account the viscosity effects due to temperature and concentration variations.

ρ_{0f} in Eq. (1.9) and μ_{0f} in Eq.(1.11) are both related to the reference conditions for the hydraulic head φ_0 , the concentration C_0 and the temperature T_{0f} .

$\frac{\rho_f - \rho_{0f}}{\rho_{0f}}$ represents the buoyancy term and can be easily derived from of the EOS for ρ_f .

Equation 4: Energy conservation of the fluid and solid.

$$\frac{\partial}{\partial t}(\phi\rho_f c_f T_f) + \text{div}(\rho_f c_f T_f \mathbf{q}) + \text{div}(\bar{\mathbf{j}}_f^{*T}) - \text{div}(\lambda^{\text{disp}}_f \mathbf{grad}(T_f)) = Q^T_f \quad (1.12)$$

In the averaging the term $\sigma \text{div}(\mathbf{V}^*)$ (rate of internal energy production due to surface force) has been neglected. c_f is the fluid heat capacity and T_f is the fluid temperature.

$$\bar{\mathbf{j}}_f^{*T} = -\phi \bar{\lambda}_f^{\text{cond}} \mathbf{grad}(T_f) \quad (1.13)$$

$\bar{\lambda}_f^{\text{cond}}$ tensor of heat conduction of the fluid occupying the void space of a porous medium.

$-\lambda^{\text{disp}}_f \mathbf{grad}(T_f)$ expressed the dispersive heat flux resulting from fluctuations in \mathbf{V}^* and T_f in the pore space. λ^{disp}_f is referred to as tensor of thermal dispersion and conceptually can be considered similar to the mechanical dispersion tensor seen in (1.3)

The macroscopic heat balance equation for the solid phase is:

$$\frac{\partial}{\partial t}((1-\phi)\rho_s c_s T_s) + \text{div}(\bar{\mathbf{j}}_s^{*T}) = Q^T_s \quad (1.14)$$

where Q^T_s is a heat supply, c_s is the solid heat capacity, T_s is the solid temperature and

$$\bar{\mathbf{j}}_s^{*T} = -(1-\phi)\bar{\lambda}_s^{\text{cond}} \mathbf{grad}(T_s) \quad (1.15)$$

is the conductive heat flux in the solid. $\bar{\lambda}_s^{\text{cond}}$ is named tensor of thermal conductivity of the solid porous matrix.

Because solid grains are relatively small and fluid velocity in the void space is small, solid and liquid phase can be considered in thermal equilibrium, i.e. $T_f = T_s = T$. Therefore summing equation (1.12) and (1.14) the heat equation balance for a porous medium as a whole can be obtained.

$$\boxed{\frac{\partial}{\partial t} \left(\underbrace{\left(\phi\rho_f c_f + (1-\phi)\rho_s c_s \right)}_M T \right) + \text{div}(\rho_f c_f T_f \mathbf{q}) - \text{div}(\lambda \mathbf{grad}(T)) = Q^T} \quad (1.16)$$

where

M in the r.h.s. underbrace is often referred to as accumulation term for the heat.

Q^T is the heat supply and

$$\lambda = \underbrace{\phi \bar{\lambda}_f^{\text{cond}} + (1-\phi)\bar{\lambda}_s^{\text{cond}}}_{\bar{\lambda}_p^{\text{cond}}} + \lambda^{\text{disp}} \quad (1.17)$$

λ is the thermodispersion tensor, in which the coefficient in the underbrace, λ_p^{cond} is the thermal conductivity of the saturated porous medium as a whole. The coefficient of thermal dispersion λ^{disp} can be neglected with respect to λ_p^{cond} as shown in Bear (1988).

$-\lambda \mathbf{grad}(T)$ combines the conductive heat flux in the fluid and in the solid, and the dispersive heat flux in the fluid.

By observing (1.5) and (1.16) it results that solute is transported at the pore velocity $\frac{\mathbf{q}}{\phi} = \mathbf{V}^*$

while the heat transport is retarded due to the heat exchange between the fluid and the solid grains (M , accumulation term for the heat). For a given Darcy velocity \mathbf{q} the velocity of the advective thermal front is

$$\mathbf{V}_T = \frac{\rho_f c_f \mathbf{q}}{M} = \mathbf{V}^* \underbrace{\frac{\phi \rho_f c_f}{M}}_{1/R} \quad (1.18)$$

Oldenburg and Pruess (1999) estimated that for an hydrothermal convective system the retardation factor R appearing in (1.18) is approximately 7, i.e. the thermal front will move at 1/7 the speed of the solute front.

The equation of state for the fluid density (1.19) and one for the fluid viscosity (1.20) have to be added:

$$\boxed{\rho_f = \rho_{f0} \left(1 + \bar{\gamma}(p_f - p_{f0}) - \bar{\beta}(T_f - T_{f0}) + \bar{\alpha}(C_\alpha - C_{\alpha0}) \right)} \quad (1.19)$$

where $\rho_f = \rho_{f0}$ for $p_f = p_{f0}$, $T_f = T_{f0}$ and $C_\alpha = C_{\alpha0}$

$\bar{\gamma}$, $\bar{\beta}$ and $\bar{\alpha}$ are the coefficient of compressibility, the coefficient of thermal expansion and the mass concentration ratio respectively.

For the fluid viscosity

$$\boxed{\mu_f = \mu_f(C, T)} \quad (1.20)$$

where the concentration and temperature dependencies are determined by empirical polynomial relationships (Hassanizadeh and Leijnse 1988).

In the end, six equations in six dependent variables: $\mathbf{V}^*, \rho_f, \mu_f, C, p_f, T$ are defined: four balance equations ((1.1) (1.8) (1.5) (1.16)) and two equations of states for ρ_f and μ_f . To complete the mathematical statement of heat and mass transfer problem appropriate initial and boundary conditions must be added.

Nomenclature

c	heat capacity (fluid or solid).	$L^2 T^2 \Theta^{-1}$
C	concentration of the solute.	$M L^{-3}$
\mathbf{D}	hydrodynamic dispersion tensor. concentration of the considered α specie.	$L^2 T^{-1}$
$\bar{\mathbf{D}}_{diff}$	molecular diffusion of the saturated porous media.	$L^2 T^{-1}$
\mathbf{D}_{disp}	mechanical dispersion tensor.	$L^2 T^{-1}$
\mathbf{g}	vector of gravity acceleration.	$L T^{-2}$
\mathbf{j}^*	diffusive flux relative to the mass average velocity.	$M L^2 T^{-1}$
\mathbf{k}	permeability.	L^2
\mathbf{K}	hydraulic conductivity tensor.	$L T^{-1}$
M	Heat accumulation term	$M L^{-1} T^{-2} \Theta^{-1}$
Pe_D	Peclet number.	1
p_f	fluid pressure.	$M L^{-1} T^{-2}$
\mathbf{q}	Darcy velocity.	$L T^{-1}$
$Q_{Boussinesq}$	Boussinesq term.	$M L^{-3} T^{-1}$
Q	sink/source term.	$M L^{-3} T^{-1}$
R	Retardation factor	1
S_0	medium storativity.	L^{-1}
T	temperature.	Θ
\mathbf{V}^*	pore velocity	$L T^{-1}$

Greek symbols

$\bar{\alpha}$	mass concentration ratio.	1
$\bar{\beta}$	coefficient of thermal expansion.	Θ^{-1}
$\bar{\gamma}$	coefficient of compressibility.	L^{-1}
λ	thermodispersion tensor.	$M L T^{-3} \Theta^{-1}$

$\bar{\lambda}_f^{\text{cond}}$	tensor of heat conduction of the fluid occupying the void space of a porous medium.	$M L T^{-3} \Theta^{-1}$
λ_f^{disp}	tensor of thermal dispersion.	$M L T^{-3} \Theta^{-1}$
$\bar{\lambda}_s^{\text{cond}}$	tensor of thermal conductivity of the solid porous matrix.	$M L T^{-3} \Theta^{-1}$
μ	dynamic fluid viscosity.	$M L^{-1} T^{-1}$
ρ_f	density of the fluid system.	$M L^{-3}$
ϕ	porosity.	1
φ	piezometric head or Hubbert potential	L
σ	stress tensor.	$M L^{-1} T^{-2}$

Subscript

f	fluid.
s	solid.
0	reference values of the considered property.