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**Equilibrium and Transfer
in Porous Media 2**

Transfer Laws

Jean-François Daïan

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Félix Darve

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Nomenclature

** Notations marked * can have several different meanings. In general, their meaning will be clear from om the context in which they are used.*

Notation	SI Unit	Name	Reference (volume)-section, [Equation]
A, B, C, \dots		arbitrary constants	
A	$\text{m}^{-1} (\text{m}^2/\text{m}^3)$	specific surface of a porous medium*	(I)-4.2.2.1, 1.4.2.2
c, C_k	kg/kg	concentration, mass fraction	1.2.2.3
C	$\text{J K}^{-1} \text{m}^{-3}$	volume thermal capacity (per unit volume)	1.2.3
$\overline{\overline{C}}$	m^{-2}	inverse of permeability tensor	1.5.4.3
d	m	pore diameter	
d_c	m	characteristic (critical) pore diameter	2.1.2.2
d_h	m	hydraulic diameter	1.4.2.2
$D_k, D_0,$ $\overline{\overline{D}}_{ef}, D_{ef}$	$\text{m}^2 \text{s}^{-1}$	diffusion coefficients or tensors	1.2.2.1, 1.2.2.3, [1.7] 1.4.3.2, [1.26]
D_θ	$\text{m}^2 \text{s}^{-1}$	hydric diffusivity	2.2.2.4, [2.26], 2.2.3
D_T, D_T^*	$\text{m}^2 \text{s}^{-1}$	thermal diffusivity (pure, apparent)	2.2.3
$\overline{\overline{D}}_k^{disp}$	$\text{m}^2 \text{s}^{-1}$	dispersion tensor of the component k	1.4.3.4, [1.27]
$\overline{\overline{D}}$	s^{-1}	strain rate tensor	1.5.2.1

E_k	$\text{m}^2 \text{s}^{-1}$	effusion coefficient of the component k	2.3.2.5, [2.48]
g_k, \bar{g}_k	$\text{mole m}^{-2} \text{s}^{-1}$	density of molar flux*	1.2.2.1, [1.3]
g	m s^{-2}	gravitational field*	
g	variable	“conductance”	1.5.7.2
h h_ρ h_T	variable m s^{-1} $\text{J m}^{-2} \text{s}^{-1} \text{K}^{-1}$	exchange coefficient	2.2.1.3, [2.14]
\bar{J}_X	$X \text{ m}^{-2} \text{s}^{-1}$	flux density of the value X	1.4.1.2
$J, \bar{J}_k, \bar{J}_\alpha$	$\text{kg m}^{-2} \text{s}^{-1}$	mass flux density, of the component k , of the α -phase	1.2.2.2, 1.5.2.3, [1.48]
\bar{j}_k	$\text{kg m}^{-2} \text{s}^{-1}$	diffusive mass flux density of the component k	1.2.2.2, 1.4.1.3, [1.21]
k, \bar{k}	m^2	intrinsic permeability (tensor)	1.4.2.1, [1.22]
K_l \hat{K} K	$\text{m}^2 \text{Pa}^{-1} \text{s}^{-1}$ m s^{-1} $\text{m}^2 \text{Pa}^{-1} \text{s}^{-1}$	hydraulic conductivity hydraulic conductivity “hydraulic conductivity”	2.2.2.2, [2.19] 2.2.2.2, [2.21] 2.2.2.3, [2.23] 2.2.3, [2.30]
l_m	m	molecular mean free path	2.1.2.1
L_v	J kg^{-1}	heat of vaporization	(I)-2.4.3.2
M	kg mole^{-1}	molar mass	
N, N_k	mole kg^{-1}	number of moles per unit mass	1.5.2.3
n, n_k	moles m^{-3}	molar concentration of a gas, of a component	(I)-2.4.1.1, 1.2.2.1
\bar{n}	-	normal unit vector	
P	Pa	pressure	
P_c	Pa	capillary pressure	(I)-1.2.3, [1.1]
Pe	-	Péclet number	1.4.3.4, [1.28]
Q	$\text{m}^3 \text{s}^{-1}$	volume flow rate	
q, \bar{q}	$\text{J m}^{-2} \text{s}^{-1}$	density of thermal conductive flux	1.2.3, [1.9]
R	$\text{J mole}^{-1} \text{K}^{-1}$	ideal gas constant	
R_c	m	interfacial curvature radius	(I)-1.2.3, [1.1]
Re	-	Reynolds number	1.2.1.3
S	$\text{J K}^{-1} \text{kg}^{-1}$	specific entropy*	1.5.2.1, footnote 32
S	m^2	section*	
S_X	$X \text{ m}^{-3} \text{s}^{-1}$	volume source for the value X	1.4.1.2
s	$\text{J K}^{-1} \text{m}^{-3}$	volume concentration of entropy*	1.5.2.2

t	s	time, date	
T, \hat{T}	K	Kelvin temperature, Celsius temperature	
U	J kg^{-1}	specific internal energy	1.5.2.1, footnote 32
u	J m^{-3}	volume concentration of internal energy*	1.5.2.1, footnote 32
V	m s^{-1}	flow velocity, Darcian velocity	1.2.1, 1.4.1.3
V_f	m s^{-1}	velocity of the fluid phase	1.5.3.1, [1.57]
v_i	m s^{-1}	Cartesian coordinate of flow velocity	1.5.1.3
\bar{v}	m s^{-1}	average molecular velocity	2.3.2.1, [2.41]
x, y, z, x_k	m	Cartesian coordinates*	
x, x_i	-	mole fraction*	(I)-2.4.4.1, 2.3.2.7
X	X m^{-3}	volume concentration of the value X	1.4.1.2
z	m	descending vertical coordinate	
		GREEK SYMBOLS	
α	-	wetting angle*	(I)-1.2.2 ; (I)-2.1.4
α	K^{-1}	coefficient of thermal variation*	
α	$\text{m}^2 \text{s}^{-1}$	diffusivity, (particularly thermal)*	1.2.3
β_D	-	Knudsen factor	2.1.2.2
β_K	-	Klinkenberg factor	2.1.2.3
$\chi_\alpha, \gamma_\alpha, \zeta_\alpha$	-	EMT coefficients	1.5.7.1, 2.3.4.1
δ, δ_{ij}	-	unit tensor, Kronecker symbol	
ε	-	porosity	(I)-1.2.4.2
ε_α	-	volume fraction of the phase α	1.3.2.3, [1.12] 1.4.1.2, [1.17]
Γ	variable	capacity	2.2.1.2, [2.13]
Γ_c	Pa^{-1}	capillary capacity	2.2.2.1, [2.17]
$\hat{\Gamma}_c$	m^{-1}	capillary capacity	2.1.2.2
Γ_φ	-	hygroscopic capacity	2.2.2.4, [2.27]
γ, γ_k	-	capacity in relation to the component k	2.2.6.1, [2.37]
$\eta(d)$	-	cumulative pore size distribution	(I)-3.1.1.2,
κ_w, κ_n	-	relative permeabilities	2.1.1.3, [2.2]
λ, Λ	$\text{J m}^{-1} \text{s}^{-1} \text{K}^{-1}$	thermal conductivity	1.2.3, [1.9]
A^*	$\text{J m}^{-1} \text{s}^{-1} \text{K}^{-1}$		
A^*			

μ	Pa.s	dynamic viscosity	1.2.1.1
μ_k	J mole ⁻¹	chemical potential of the component k	(I)-2.4.4.1, [2.35] 1.5.2.3
θ θ_s	- -	liquid volume fraction, volume saturation	(I)-1.2.4.2
θ_r^w, θ_r^n	-	residual saturations	(I)-3.1.2.2 2.1.1
ρ ρ_s	kg m ⁻³ kg m ⁻³	density, mass concentration	
σ	N m ⁻¹	interfacial tension* (particularly capillary)	(I)-1.2.3, [1.1] ; (I)-2.1.2 (I)-2.1.5.1
σ	variable	transport capacity, "conductivity"*	1.5.7.1, 2.3.4.1
τ, τ, τ_{ij}	Pa	constraint, constraint tensor*	1.2.1.1
τ, τ, τ_{ij}	-	coefficient, tortuosity tensor*	1.4.3.2, [1.26] 1.5.4.1, [1.68]
Ω	m ³	volume	
ξ, η, \dots	variable	silent variable in an integration, silent argument of a function	
Ψ $\hat{\psi}$	Pa m	capillary potential capillary potential	(I)-1.2.3, [1.1] 2.1.2.2

Subscripts and superscripts	
a	atmosphere, air
at	standard atmosphere
bd	boundary
c	capillary
ef	effective
eff	effusion
f	fluid
g	gas
ini	initial
$i, j \dots$	index of direction in Cartesian coordinate system
$k, l \dots$	index of a component in a mix

l	liquid
m	mean
s, sat s s	saturated, at saturation* solid*
v	Vapor
vs	saturated vapor
v	Viscous
w, n	wetting, non-wetting*
α	index of a phase in composite medium or in porous medium

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Chapter 1

Transport and Transfer: from Homogeneous Phases to Porous Media

This introductory chapter, devoted to the physical and conceptual basics of the laws of transport in porous media might seem extremely long to a reader understandably anxious to “get down to the nitty gritty” of the subject. There is no real problem if readers wish to briefly skim through it, simply refreshing their memories, if need be, about the essential concepts relating to transfers (Appendix 1.5.1) and the typical laws governing transfer in homogeneous phase (section 1.2), and look at section 1.4 on balances and elementary transfer laws in porous media.

1.1. Transfer phenomena: complementary approaches

1.1.1. *Transfer processes and couplings*

In this and the following chapters, we shall discuss three fundamental transfer phenomena¹ which can occur in a porous medium:

– Transport by *flow* of fluids with invariable chemical composition. The particular problems posed by the flow of gases will be dealt with in Chapter 2.

¹ We are omitting certain transfer processes: in particular, chemical reactions and the accompanying energy transfers, along with electrochemical phenomena, ionic transport under the influence of an external electrical field and thermo-electrical processes.

– *Diffusion* in a fluid with variable chemical composition. Apart from the possible overall fluid transfer, we need to discuss the transport of each of its components. We distinguish between diffusion of dissolved matter in the liquid phase and diffusion within multi-component gases. Transport by diffusion in the gaseous phase, like the flow of gases, raises particular questions in porous media, which we shall examine in Chapter 2.

– Heat transfer by *conduction* with variable temperature.

The phenomena of *phase-change*, which play a major role in all our subsequent discussions, are not cited here as being among the fundamental transfer processes. Although they represent a transfer of matter between phases, it is generally held that the dynamics of these changes is not governed by a specific law. The thermodynamic relations for polyphasic systems at equilibrium, such as Kelvin’s law which, in porous media, links partial vapor pressure to the pressure of the liquid (Chapter (I)-1, section 1.3.2), are supposed to be applicable locally and instantaneously during the transfer processes.² This is one of the aspects of the generally-accepted hypothesis of *local equilibrium*, which we shall discuss further later on. According to this hypothesis, phase-change accompanies other transfer phenomena, and these other phenomena impose their own dynamics on the process.

Each of the aforementioned three transfer processes can, in specific conditions, occur on its own, in a homogeneous phase or within a porous medium. However, in many circumstances, they take place simultaneously, and also interact with one another. In the interests of clarity of this discussion, we begin by formulating the transfer law for each of the processes in its “pure” form. Secondly, we examine the forms of coupling which are liable to link the processes to one another and the transfer laws. With regard to porous media, in Chapter 2 we shall give the laws of *isothermal transport*, without heat transfer. We begin by separately discussing transport in each of the fluid phases. The coupling which results from local equilibrium when a volatile liquid partially occupies the pore space will then be discussed. In Chapter (III)-2, we examine primarily the coupling which occurs, in the same conditions of occupation of the pore space, between conductive heat transfer and transport of matter by flow and diffusion.

The approach advocated by the *thermodynamics of irreversible processes* (TIP), on the other hand – both for porous media and homogeneous phases – is to directly

² However, in practice, this hypothesis can be disregarded, *a priori*. It is possible to apply the TIP approach to the formulation of a specific law for the dynamics of phase-change. J.-C. Benet devoted his thesis to this subject, [BEN 81] and some of his later work also focuses on it. This question can also be viewed from the perspective of molecular dynamics, J. H. De Boer [DE 68].

deal with situations where all the processes take place simultaneously. The “entropy balance” method aims to use only the fundamental principles of dynamics and thermodynamics as a basis on which to establish the expression of the transfer laws for processes considered to be interactive, *a priori*. A single approach gives us both the laws for the “pure” phenomena and the coupling that occurs between them. In the appendix to this chapter (section 1.6 for homogeneous phases and 1.7 for porous media), we give a partial overview of the TIP approach, but it will not be adopted systematically. Indeed, to our knowledge, the proponents of TIP, while they have dealt with significant aspects of transfers in porous media³, have not used this approach to deal with all the phenomena which we wish to focus on particularly in this book.

1.1.2. *Continuums and molecular aspect*

To formulate the laws which govern transfers in homogeneous phases, two main types of approach can be employed: largely *axiomatic* approaches, based on the notion of a *continuum*, and approaches based on *statistical mechanics*, which deals with systems formed by a large number of molecules with chaotic motion.

1.1.2.1. *Continuums and axiomatic approach*

The so-called *axiomatic* approaches define the concept of a continuum to describe moving and evolving matter. This category includes traditional *fluid dynamics* as well as classic thermodynamics, from which the *thermodynamics of irreversible processes* (TIP) derives; TIP is used for the study of transfers.

In the context of these approaches, each point or element of volume of the material is characterized by a certain number of *state variables*, defined in earlier chapters in the context of thermodynamics of equilibrium states⁴: pressure, density, possibly the concentration of the different components, temperature, etc.

Also, at each point, we define *densities of flux* – usually vectorial flux, of varying types: mass flux, material flux, energy flux, etc. The concept of flux is the specific hallmark of transfer processes and of their kinetics.

The appendix (section 1.5.1.1) gives a reminder of the fundamental formalism relating to the field of variables, fluxes and balances, which is crucial for the study of transfers, both in homogeneous phases and in porous media.

³ In particular, see Olivier Coussy [COU 91].

⁴ This could more accurately be called *thermostatics*. It is only now, with transfers taken into account, that we are truly dealing with *thermodynamics*!

The *transfer laws*, or *behavioral laws*, express the relations between the densities of flux and the field of state variables – particularly their gradient. The balance equations which express the *principles of conservation* of mass and energy, and the transfer laws both belong to the *constitutive equations* for the processes. By eliminating fluxes between these two types of constitutive equations, we obtain spatial and temporal partial differential equations which apply to the state variables.

In order to formulate the behavioral laws on a theoretical basis, we need to use the fundamental principles (or *axioms*) of dynamics and thermodynamics, including the conservation laws, in particular. The most axiomatic approach is TIP. TIP practically uses only the fundamental principles to explain the general form of the transfer laws. However, it is generally not capable, on its own, of yielding operational transfer laws, or of a quantitative estimation of the coefficients involved. The axiomatic approach must be supplemented with experimental practice, or else we need to integrate elements which are foreign to the concept of a continuum, taken from the molecular approach.

1.1.2.2. *The contribution of statistical molecular physics*

The thermodynamics of equilibrium states has already shown us that analysis in terms of a continuum can hardly do without the illumination given by the molecular approach, and in some cases must give way to it entirely. Thus, the notion of pressure defined axiomatically in connection with the first law of thermodynamics (Chapter (I)-2, section 2.2.2) is greatly enriched by the view of pressure in molecular analysis (Chapter (I)-2, section 2.4.1.1). In the domain of transfers, the gas transport laws relating to flow or diffusion which stem from the continuum approach prove inadequate in certain circumstances, when we have to use a molecular approach (Chapter 2, section 2.1.2).

Statistical mechanics is the theory of matter considered as a collection of molecules with disordered movements. For systems made up of a very large number of molecules in a state of equilibrium, a certain number of stable statistical properties can be noted, in spite of the molecular disorder. The statistical approach uses the molecular point of view as the basis for the notions which the continuum approach bases on axioms, thereby giving them meaning and enriching them.

The *kinetic theory of gases* is the branch of statistical mechanics which deals with ideal gases. It constitutes a coherent whole which, without having to introduce too many arbitrary hypotheses, yields results that correspond to those of conventional thermostatics. In addition, statistical examination provides data such as the molecular velocity distribution function at equilibrium, which conventional thermodynamics is obviously unable to take into account. The statistical data not