

CIVIL ENGINEERING AND GEOMECHANICS SERIES



# **Equilibrium and Transfer in Porous Media 1**

*Equilibrium States*

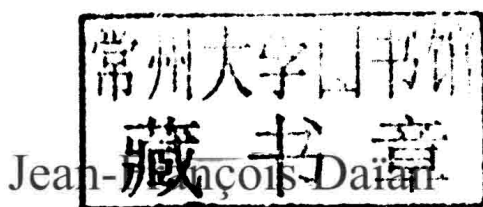
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**ISTE**

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# Equilibrium and Transfer in Porous Media 1

*Equilibrium States*



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## Equilibrium and Transfer in Porous Media 1



## Foreword

The understanding of porous media transport phenomena is a challenging intellectual task and, therefore, makes the writing of a pedagogically sound textbook very difficult.

On the one hand, practical models require addressing the multiple-scale aspects characteristic of porous media problems. Pore-scale physics generally calls for the usual technical student background in transport phenomena. However, multiphase aspects and the associated physics of interfaces make it difficult to deal with such problems for *traditional* university and school training. We easily understand that developing macro-scale models, from such a complicated micro-scale physics, that is useful for dealing with usual engineering problems is an intricate issue. Indeed, while sophisticated mathematical tools have been developed in the past decades (the various brands of volume averaging, homogenization theory, stochastic methods, etc.), it is symptomatic that many models currently used in practice are still of a heuristic nature. The case of multiphase flow with the use of generalized Darcy's laws or its avatar, the Richards equation, is a good example: assumptions for recovering such models from usual upscaling techniques are too drastic to be entirely satisfactory. For obvious reasons, this is also the case for highly coupled, nonlinear problems. Research continues on these topics, while engineering practice still greatly makes use of *traditional*, heuristic models. For scientists to sometimes have such a lack of confidence on the model they use is not completely unknown in other fields, but it seems that this is particularly marked in porous media physics. We will return to the pedagogical implications of such a difficulty later in this foreword.

On the other hand, porous media applications span over many different fields: chemical, petroleum, civil and mechanical engineering, biomechanics, hydrogeology and environmental hydrogeology, to name a few. This of course raises another difficulty when writing a textbook. Indeed, there is a wide range of scales and mechanisms involved, with a huge diversity of modeling targets. It is not absolutely

surprising that most available textbooks dealing with transport phenomena in porous media have a coloration of some sort: civil engineering, hydrogeology, petroleum engineering, etc. Someone interested in applications not covered by these dedicated textbooks may find this book more difficult to read.

The two above-mentioned major difficulties require pedagogical choices to be made. If one wants to produce a textbook useful for an audience of undergraduate or graduate students, engineers, and even scientists in the field who may want to discover applications or problems outside their area of expertise, he/she must have a solution: (1) between models strongly supported by upscaling techniques and heuristically based models, and (2) in terms of the targeted audience. This book does not pretend to be an encyclopedia about porous media physics. Therefore, it does not cover everything. First, this is not a research book. The readers will not find a comprehensive presentation, for instance, of upscaling techniques, nor will they find an extensive literature review. This book, as already suggested above, fits into the category of textbooks. Although all the application fields are not covered, the book's originality is precise in that it is not targeted toward a strongly identified specific audience. Hence, it has a strong potential for being useful for people coming from very different backgrounds.

As already mentioned, one cannot bypass the multi-scale aspect inherent to porous media physics. Previous attempts to do so have led readers to misleading conceptions (the concept of tortuosity is a good example) or have failed to emphasize the exact nature, particularly exchange terms, of some terms in the macro-scale equations. It is also evident that, for a textbook, and because used macro-scale models often have their own justification outside such upscaling theory, the authors have to propose a mixture of approaches. This book makes an extensive use of pore-scale physical description, which offers the readers a solid ground based on the skill set of average undergraduate students. Classical multiphase, multicomponent physics is presented, with a careful description of interfacial phenomena, capillary and thermodynamic equilibrium. Emphasis is also put on particular and original aspects, for instance sorption phenomena and gel physics, which are not often described at length or not described at all in other textbooks. Upscaling aspects are not overlooked. A small amount of volume averaging technique is proposed to explain the relationship between pore-scale and macro-scale models. Meso-scale approaches, such as percolation theory, are called upon to explain some intricate multiphase flow patterns, which are difficult to describe from a pure single pore view. Of course, ample space is kept for models that are largely used, while sometimes lacking the support of rigorous upscaling theories. The preliminary comprehensive lower scale analysis proposed in the book ensures that these models are not considered in an absolute and dogmatic manner, hence raising awareness for avoiding potential misuses.

This book provides a detailed analysis of the aspects required for the understanding of many experimental techniques, something that is often overlooked in other textbooks. Entire chapters are devoted to porosimetry and sorption isotherm measurements, which, along with many proposed exercises, provide the readers with a good opportunity to address practical problems and facilitate the learning process.

Ultimately, readers will have a textbook at their disposal, which is very useful to start understanding porous media physics and deal with, in a very effective manner, the most classical transport phenomena: one-phase and multiphase flows, sorption, heat transfer, coupled transport mechanisms and, in particular, drying, which is dealt with in a comprehensive manner, which is not the case in most other textbooks.

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January 2014





## Nomenclature (Volume 1)

*The notation marked with \* can be used with a variety of meanings. Usually, the context should prevent any confusion.*

Notation	SI unit	Name	Reference (section, [equation])
$A, B, C, \dots$		Undefined constants	
$A$	$\text{m}^2$	Surface area of interface*	2.1.5.1
$A$	$\text{m}^{-1} (\text{m}^2/\text{m}^3)$	Specific surface of a porous medium*	4.2.2.1
$A(d)$	$\text{m}^{-1} (\text{m}^2/\text{m}^3)$	Distribution of the specific surface*	4.2.3.1, [4.9]
$a$	-	Chemical activity	2.4.5.4
$c_v$	$\text{J K}^{-1} \text{mole}^{-1},$ $\text{J K}^{-1} \text{kg}^{-1}$	Specific heat at constant volume (per mole or per unit mass)	2.4.2.4
$c_p$	$\text{J K}^{-1} \text{mole}^{-1},$ $\text{J K}^{-1} \text{kg}^{-1}$	Specific heat at constant pressure	2.4.2.4
$d$	m	Pore diameter	
$e$	m	Thickness of adsorbed film	4.2.2.1, [4.5]
$F$	J	Free energy	2.4.2.3, [2.28]
$G$	J	Free enthalpy	2.4.2.3, [2.29]
$g$	$\text{J mole}^{-1},$ $\text{J kg}^{-1}$	Specific free enthalpy* (per mole or per unit mass)	
$g$	$\text{m s}^{-2}$	Acceleration due to gravity*	
$H$	J	Enthalpy	2.4.2.3, [2.27]
$L_v$	$\text{J kg}^{-1}$	Heat of vaporization (per unit mass)	2.4.3.2
$L_\pi$	$\text{J kg}^{-1}$	Heat of adsorption at constant	2.1.5.7, [2.13]

		two-dimensional pressure (per unit mass)	
$L_{n_s}$	$\text{J kg}^{-1}$	Isosteric adsorption heat (per unit mass)	2.1.5.7, [2.14]
$L_{sl}$	$\text{J kg}^{-1}$	Heat of fusion (per unit mass)	2.3.1
$M$	$\text{kg mole}^{-1}$	Molar mass	
$N, N_i$	mole	Number of moles	2.4.2.1, 2.4.4.1
$n$	$\text{moles m}^{-3}$	Molar concentration of a gas	2.4.1.1, 2.4.1.2
$n_s$	$\text{moles m}^{-2}$	Surface molar concentration of an interface	2.1.5.1, [2.5]
$P$	Pa	Pressure	2.4.1
$P_c$	Pa	Capillary pressure	1.2.3, [1.1]
$P_{\text{int}}$	Pa	Internal pressure	2.4.1.2, [2.25]
$Q$	J	Heat	2.4.2.2
$R$	$\text{J mole}^{-1} \text{K}^{-1}$	Ideal gas constant	
$R_c$	m	Radius of curvature	1.2.3, [1.1]
$S$	$\text{J K}^{-1}$	Entropy	2.4.2.2, [2.26]
$s$	$\text{J K}^{-1} \text{mole}^{-1}$ , $\text{J K}^{-1} \text{kg}^{-1}$	Specific entropy (per mole or per unit mass)	
$T$	K	Temperature (Kelvin)	
$U$	J	Internal energy	2.4.1.1, 2.4.2.2, [2.26], 2.4.4.1, [2.35]
$u$	$\text{J mole}^{-1}$ , $\text{J kg}^{-1}$	Specific internal energy (per mole or per unit mass)	
$V$	$\text{m}^3$	Volume	
$v$	$\text{m}^3 \text{mole}^{-1}$ , $\text{m}^3 \text{kg}^{-1}$	Specific volume (per mole or per unit mass)	
$W$	J	Work	2.4.2.2
$x, x_i$	-	Molar fraction	2.4.4.1
$\alpha$	-	Wetting angle*	1.2; 2.1.4
$\alpha$	$\text{K}^{-1}$	Thermal variation coefficient*	4.1.1.1
$\varepsilon$	-	Porosity	1.2.4.2
$\eta(d)$	-	Cumulative porometric distribution	3.1.1.2
$\Phi$	$\text{J kg}^{-1}$	Thermodynamical potential	1.3.2, 2.2.1.2, [2.16], [2.17]

$\varphi$	-	Vapor saturation rate	1.3.2, [1.4]
$\mu$	J mole <sup>-1</sup>	Chemical potential*	2.4.4.1, [2.35]
$\pi$	N m <sup>-1</sup>	Two-dimensional pressure	2.3.3, [2.3], 2.1.5.6
$\theta$	-	Liquid volume fraction, saturation	1.2.4.2
$\rho$	kg m <sup>-3</sup>	Density, mass concentration	
$\sigma$	N m <sup>-1</sup>	Interfacial tension	1.2.3, [1.1], 2.1.2, 2.1.5.1
$\Psi$	Pa	Capillary potential	1.2.3, [1.1]
$\Psi_{ls}$	Pa	Cryogenic depression	2.3.1, [2.21]

Subscripts and Superscripts	
$a$	Ambient, air
$at$	Standard atmosphere
$c$	Capillary
$g$	Gas
$l$	Liquid
$lv$	Liquid–vapor
$n, w$	Non-wetting, wetting*
$os$	Osmotic
$s$	Solid*
$sl$	Solid–liquid
$sv$	Solid–vapor
$v$	Vapor
$vs$	Saturated vapor
$w, n$	Wetting, non-wetting



## Introduction

# Porous Media and What Happens within Them

### I.1. Defining porous media

A porous medium is composed of a *solid matrix* and its geometrical complement: the *pore space*. This pore space can be occupied by one or more fluids.

At this point, we can (already) make a distinction between *granular* porous media and *consolidated* porous media. The typical granular porous medium is a pile of glass beads or grains of sand. In limestone or concrete, which can be used as examples of consolidated porous media, the pore space is “hollowed out” of the solid matrix. The usual vocabulary is not very appropriate here, as the word “granular” refers to morphology and the solid phase’s lack of connectivity, whereas the word “consolidated” suggests a cohesion within the porous medium. In limestone or concrete, the cohesion is that of the solid phase, as a result of its connectivity. At least in the case of concrete, microscopic examination shows that there is less “true connectivity” than a structured overlap of solid elements. The granular piles can also show a cohesion which, in this case, comes from the intergranular forces, and especially from the interactions of the grains with the interstitial fluids that act as glue. The pore space is obviously connected for the granular piles. On the other hand, in the “consolidated” porous media, the pore space may be made up of cavities that are not mutually connected (called *closed porosity*), either partially or even completely, in the case of foams and other expanded products.

However, the physics of porous media has less to do with their structure than with the varied phenomena that can be observed within them. Fluids within the pore space can be liquid or gaseous, or can even be likely to produce an additional solid phase by freezing or by precipitation of a dissolved component. They may or may not be chemically pure, containing minerals or organic particles, or even living micro-organisms. Chemical reactions can take place in fluids or in the solid matrix. Physicochemical interactions between the matrix and fluids can take place.

The term pore space does not exempt us from discussing the definition of the word “pore”, often found in the frequently used expression “at the scale of a pore” and in the common classification that distinguishes *micropores*, *mesopores* and *macropores*. Defining “pore” as the elementary component of the *pore space* is a serious topological problem. Assuming it is solved, we can attribute a size to the object thus defined, and delimit the range of the sizes of what is called “pore”, according to criteria yet to be defined.

Any criterion that defines a pore is intrinsically linked to the phenomena that are likely to occur within it. It is not hard to assign a lower limit to the size of micropores: this is the size of the smallest molecules of a fluid that can be found within it, or the typical range of the van der Waals forces. Let us speak about, for example, the diameter of the water molecule which is 3 Å. A pore of this size is more deserving of the name *absorption site* used by chemists. This remains in the domain of *micropores* as long as they are cavities that can only contain a few units of small molecules of fluid, roughly up to 3 nm. These reduced molecule populations do not deserve the name *fluid phase*; their study belongs to the domain of *molecular dynamics*. The properties of the fluid, for example, viscosity or interfacial tension, to which these molecules normally belong, are no longer pertinent in such pores. Even the notion of pressure becomes problematic, and the intermolecular force exerted by the solid wall plays an essential role in the behavior of the populations of molecules.

We enter into the domain of *mesopores* when the size is sufficient to contain an actual liquid phase. The liquid contained in these pores is called *capillary*, which means that its state (pressure) is directly linked to the *interfacial tension* of the liquid that exists at the interface with the surrounding atmosphere, and to the shape of the latter. The expression *capillaro-porous*, used notably by Luikov, can be applied to porous media in which the behavior of fluids is mainly determined by the capillarity, which roughly corresponds to macro- and mesoporous bodies, excluding microporous solids. The confinement of liquids inside the mesopores, in conjunction with the capillarity, also leads to a significant decrease in vapor pressure in comparison to the saturated vapor pressure in a free state.

Again, it is the chemists studying the absorption whom we rely on for the fixing of a boundary between *meso-* and *macropores*, which is approximately 50 or 100 nm (0.1  $\mu\text{m}$ ). It is from this size of pores that, for the fluids regularly used to characterize porous media by adsorption (nitrogen or argon at low temperature, water, etc.), the pressure of the vapor upon contact with the liquid that is confined within becomes practically indiscernible from the saturated vapor pressure. The capillarity maintains its importance in the macropores and continues to determine the pressure of the liquid, but the vapor in contact is no longer significantly affected. In domains other than chemistry, as water is the most abundant liquid, this same criterion linked to the water pressure facilitates a distinction between *hygroscopic* porous media, composed in a significant part of mesopores and micropores, and therefore capable of fixing (so as not to have to choose between *absorbing*, *sorbing* and *adsorbing*) more or less liquid water in the presence of a non-saturated, humid and ambient atmosphere. On the contrary, non-hygroscopic bodies, composed solely of macropores, remain practically dry as long as no liquid water is introduced by infiltration.

This definition of macropores would create a problem for pedologists and agronomists who use the term in reference to pores of around 1 mm or even a centimeter, from cracks made by drying, or holes dug by moles in the ground. From which size do we stop talking of “pores”? The upper limit is more of a problem than the lower limit.

## 1.2. Is there a specific science of porous media?

A porous medium with fluids that it contains can be either at *equilibrium* or at *non-equilibrium*. Equilibrium can be understood from any standpoint: mechanical, thermodynamic, thermal, chemical or electrical, with the relations that they imply between the state variables. Out of equilibrium, the *transport* or the *transfer* potentially relates to all these factors, with all the couplings imaginable: filtration, diffusion, thermomigration, osmosis, electro-osmosis, etc. Whether to use the word “transport” or “transfer” is not strictly determined. “Transport” suggests the movement of fluid matter, whereas we would tend to use the term “transfer” more in the case of heat. In terms of the phenomena of molecular diffusion, it is hard to say which word is better suited. One of the most well-known journals on porous media, *Transport in Porous Media*, obviously covers thermal and chemical transfers, despite its name.

As such, can we talk of a science of porous media? The phenomena of equilibrium or transfer are the subjects of different branches of physics (mechanical



engineering and chemistry included, obviously) and in particular thermodynamics and statistical mechanics. Has everything been said now that the major laws of physics have been formulated? What is so different when these phenomena take place within a porous medium? Is it necessary to conduct a specific study?

What distinguishes equilibrium and transfers in porous media from the phenomena that are the general subject of physical science is the vital role played by the *interfaces*, omnipresent between the solid matrix and the fluids that it contains and between the fluids themselves, with the more or less complex resulting interactions. Such is the case even when we look only at the mechanical behavior of the solid matrix in isolation: the interface is the location, complex in its geometry, where the stress becomes null if the pore space is empty, or at least changes in nature if it is occupied by a fluid. On the contrary, if the main focus is on the interstitial fluids, specifically interfacial phenomena, such as capillarity, molecular adsorption of a gaseous component (or an ionic component in the liquid phase), are likely to have major importance due to the fact that each element of the volume of the porous matter can contain a considerable solid surface area – all the more if the solid matter is more finely divided. In the domain of transport, what differentiates “flow” in the usual sense of a viscous fluid from *filtration* in a porous medium is that the solid surface to which the fluid adheres at each point no longer plays the role, in the porous medium, of a simple boundary to the domain of flow. On the contrary, it is intimately mixed with all the flowing fluid volume.

Therefore, a specific protocol needs to be followed in order to deal with equilibrium and transfer phenomena when they occur within a porous medium. More generally, in physics, the objective is usually to study these phenomena when they take place in *homogeneous* phases, at least as long as we stay away from the scale of the molecule. What could be called a “science of porous media” aims to examine the specific influence of the close mixing of a solid phase and one or more fluid phases (including a vacuum) on these phenomena. It must be noted that this type of circumstance is not only encountered in the case of porous media. Foams and emulsions do not contain a solid phase, but do share with porous media the fact of being close mixes of different phases within the elementary volume, in which equilibrium, evolutions and transfers are mostly governed by interfacial phenomena. In concentrated suspensions, unlike in porous media, it is the fluid that contains the solid. Waterlogged clay passes the boundary between porous medium and suspension and the transition is marked by a radical change in rheological behavior.