MECHANICS AND PHYSICS OF POROUS SOLIDS

Mechanics and Physics of Porous Solids Olivier Coussy
© 2010 John Wiley & Sons, Ltd. ISBN: 978-0-470-72135-3

MECHANICS AND PHYSICS OF POROUS SOLIDS

Olivier Coussy

Laboratoire Central des Ponts et Chaussées
Ecole des Ponts ParisTech
Université Paris-Est
http://navier.enpc.fr/~coussy/



A John Wiley and Sons, Ltd., Publication

10.1002/9780470710388.fmatter, Downloaded from https://onlinelibrary.wiley.com/doi/10.1002/9780470710388.fmatter by Sandia National Laboratories, Wiley Online Library on [11/09/2025]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

This edition first published 2010
© 2010 John Wiley & Sons, Ltd

Registered Office
John Wiley & Sons Ltd, The Atrium, Southern Gate, Chichester, West Sussex, PO19 8SQ, United Kingdom

For details of our global editorial offices, for customer services and for information about how to apply for permission to reuse the copyright material in this book please see our website at www.wiley.com.

The right of the author to be identified as the author of this work has been asserted in accordance with the Copyright, Designs and Patents Act 1988.

All rights reserved. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, recording or otherwise, except as permitted by the UK Copyright, Designs and Patents Act 1988, without the prior permission of the publisher.

Wiley also publishes its books in a variety of electronic formats. Some content that appears in print may not be available in electronic books.

Designations used by companies to distinguish their products are often claimed as trademarks. All brand names and product names used in this book are trade names, service marks, trademarks or registered trademarks of their respective owners. The publisher is not associated with any product or vendor mentioned in this book. This publication is designed to provide accurate and authoritative information in regard to the subject matter covered. It is sold on the understanding that the publisher is not engaged in rendering professional services. If professional advice or other expert assistance is required, the services of a competent professional should be sought.

Library of Congress Cataloging-in-Publication Data

Coussy, Olivier.
Mechanics and physics of porous solids / Olivier Coussy.
p. cm.
Includes bibliographical references and index.
ISBN 978-0-470-72135-3 (cloth)
1. Porous materials. I. Title.
TA418.9.P6C683 2010
620.1′16–dc22 2009049316

A catalogue record for this book is available from the British Library.

ISBN: 978-0-47072135-3 (Hbk)

Typeset in 10/12pt Times by Aptara Inc., New Delhi, India
Printed in Singapore by Markono Print Media Pte Ltd

10.1002/9780470710388.fmatter, Downloaded from https://onlinelibrary.wiley.com/doi/10.1002/9780470710388.fmatter by Sandia National Laboratories, Wiley Online Library on [11/09/2025]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

To my wife Sandra
for putting up with it

10.1002/9780470710388.fmatter, Downloaded from https://onlinelibrary.wiley.com/doi/10.1002/9780470710388.fmatter by Sandia National Laboratories, Wiley Online Library on [11/09/2025]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

Contents

Preface **xiii**

1 The Strange World of Porous Solids **1**

2 Fluid Mixtures **11**
2.1 Chemical Potential 11
2.1.1 Free energy and chemical potential 11
2.1.2 Equilibrium of mixture composition 13
2.2 Gibbs–Duhem Equation 13
2.2.1 Derivation of the Gibbs–Duhem equation 13
2.2.2 Molar Gibbs–Duhem equation 14
2.2.3 Ideal gases 15
2.2.4 Real gases 16
2.2.5 Partial molar property 16
2.3 Ideal Mixtures 17
2.3.1 Ideal gas mixture 17
2.3.2 Ideal mixture definition 19
2.3.3 Entropy of mixing 19
2.3.4 Ideal solution – Raoult's law 21
2.3.5 Dilute ideal solution – Henry's law 21
2.3.6 Osmotic pressure 23
2.3.7 Electrostatics and excess of osmotic pressure 25
2.3.8 Reactive ideal mixture 32
2.3.9 Unconditional stability of ideal solutions 34
2.4 Regular Solutions 36
2.4.1 Regular solutions and the interaction between molecules 36
2.4.2 Conditional stability of regular solutions 37
Further Reading 40

3 The Deformable Porous Solid **41**
3.1 Strain 42
3.1.1 Deformation gradient and displacement 42

10.1002/9780470710388.fmatter, Downloaded from https://onlinelibrary.wiley.com/doi/10.1002/9780470710388.fmatter by Sandia National Laboratories, Wiley Online Library on [11/09/2025]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

	3.1.2	*Strain tensor*	43
3.2	Stress		45
	3.2.1	*The hypothesis of local contact forces*	45
	3.2.2	*The action–reaction law*	46
	3.2.3	*The Cauchy stress tensor*	47
	3.2.4	*Local mechanical equilibrium*	49
	3.2.5	*Symmetry of stress tensor*	50
3.3	Strain Work		51
	3.3.1	*Mechanical energy balance*	51
	3.3.2	*Strain work in infinitesimal transformations*	51
3.4	From Solids to Porous Solids		52
	3.4.1	*Porosity and deformation*	52
	3.4.2	*Pore pressure and stress partition*	54
	3.4.3	*Free energy balance for the fluid−solid mixture*	55
	3.4.4	*Free energy balance for the porous solid*	56
	3.4.5	*Strain work and the effective stress 'principle'*	57
	Further Reading		59
4	**The Saturated Poroelastic Solid**		**61**
4.1	The Poroelastic Solid		61
	4.1.1	*The linear poroelastic solid*	61
	4.1.2	*Microporoelasticity*	63
	4.1.3	*The nonlinear poroelastic solid*	68
4.2	Filling the Porous Solid		71
	4.2.1	*Filling by a compressible fluid*	72
	4.2.2	*Filling by a mixture containing gas bubbles − bubble pressure*	72
	4.2.3	*Undrained poroelasticity*	75
4.3	The Thermoporoelastic Solid		78
	4.3.1	*The linear thermoporoelastic solid*	78
	4.3.2	*The linear thermoporoelastic fluid−solid mixture*	79
4.4	The Poroviscoelastic Solid		80
	4.4.1	*The linear viscoelastic solid matrix*	80
	4.4.2	*The linear poroviscoelastic solid*	82
	Further Reading		83
5	**Fluid Transport and Deformation**		**85**
5.1	Transport Laws		86
	5.1.1	*Mole and mass conservation*	86
	5.1.2	*Dissipation associated with transport*	86
	5.1.3	*Fick's law*	89
	5.1.4	*Darcy's law*	90
5.2	Coupling the Deformation and the Flow		96
	5.2.1	*The Navier equation*	97
	5.2.2	*The diffusion equation*	98
5.3	Consolidation of a Soil Layer		100
	5.3.1	*Consolidation equation*	100

10.1002/9780470710388.fmatter, Downloaded from https://onlinelibrary.wiley.com/doi/10.1002/9780470710388.fmatter by Sandia National Laboratories, Wiley Online Library on [11/09/2025]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

5.3.2 Early time solution 103
5.3.3 Any time solution 103
5.3.4 Layer apparent creep 104
Further Reading 106

6 Surface Energy and Capillarity **107**
6.1 Physics and Mechanics of Interfaces 108
6.1.1 Origin of surface energy 108
6.1.2 Basic approach to van der Waals forces 109
6.1.3 Surface and interface energy 111
6.1.4 Surface energy and cohesion 113
6.1.5 Surface energy and surface stress 114
6.1.6 Wettability, angle of contact and the Young–Dupré equation 118
6.1.7 The Laplace equation 121
6.1.8 Pore invasion and interface energy change 122
6.1.9 Interface energy and adsorption 125
6.1.10 The disjoining pressure 129
6.2 Capillarity in Porous Solids 132
6.2.1 Capillary pressure curve and interface energy 132
6.2.2 Capillary rise 133
6.2.3 Porosimetry 135
6.2.4 Capillary hysteresis 136
6.3 Transport in Unsaturated Porous Solids 140
6.3.1 Relative permeability 140
6.3.2 Injection 141
Further Reading 146

7 The Unsaturated Poroelastic Solid **149**
7.1 Interface Stress as a Prestress 150
7.1.1 Interface energy and saturated poroelasticity 150
7.1.2 Adsorption-induced deformation 153
7.2 Energy Balance for the Unsaturated Porous Solid 154
7.2.1 Lagrangian and Eulerian saturations 154
7.2.2 Lagrangian saturation and free energy balance 156
7.3 The Linear Unsaturated Poroelastic Solid 159
7.3.1 Constitutive equations of unsaturated poroelasticity 159
7.3.2 Unsaturated microporoelasticity 159
7.3.3 Double porosity approach to the brittle fracture of liquid-infiltrated materials 162
7.4 Extending Linear Unsaturated Poroelasticity 164
7.4.1 The nonlinear poroelastic solid in unsaturated conditions 164
7.4.2 Accounting for interface stress effects upon deformation 165
7.4.3 The linear thermoporoelastic solid in unsaturated conditions 166
7.4.4 The linear unsaturated poroviscoelastic solid 166
Further Reading 166

10.1002/9780470710388.fmatter, Downloaded from https://onlinelibrary.wiley.com/doi/10.1002/9780470710388.fmatter by Sandia National Laboratories, Wiley Online Library on [11/09/2025]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

8	**Unconfined Phase Transition**		**167**
8.1	Chemical Potential and Phase Transition		168
	8.1.1	*Phase equilibrium law*	168
	8.1.2	*Chemical potential of a pure substance in any form*	168
	8.1.3	*Supersaturation*	171
	8.1.4	*Phase transition as an instability*	172
8.2	Liquid–Vapor Transition		175
	8.2.1	*The Kelvin equation*	175
	8.2.2	*Effect of a solute*	178
8.3	Liquid–Solid Transition		179
	8.3.1	*The Thomson equation*	179
	8.3.2	*Salt crystallization – the Correns equation*	182
8.4	Gas Bubble Formation		185
8.5	Surface Energy and Phase Transition		185
	8.5.1	*Nucleation*	186
	8.5.2	*The precondensed liquid film, the disjoining pressure and the Gibbs adsorption isotherm*	190
	8.5.3	*The premelted liquid film and crystallization*	194
	Further Reading		196
9	**Phase Transition in Porous Solids**		**197**
9.1	In-pore Phase Transition		198
	9.1.1	*Liquid saturation, pore-entry radius distribution and phase transition*	198
	9.1.2	*Spherical stress state and stability of in-pore crystallization*	201
	9.1.3	*Intermolecular forces and in-pore phase transition*	204
9.2	Kinetics and Mechanics of Drying		211
	9.2.1	*Continuum approach to drying kinetics*	211
	9.2.2	*Drying asymptotics*	215
	9.2.3	*Drying mechanics*	221
9.3	Mechanics of Confined Crystallization		223
	9.3.1	*Cryogenic swelling*	223
	9.3.2	*The hydraulic pressure*	225
	9.3.3	*Freezing and air voids*	229
	9.3.4	*Weathering and the crystallization of sea-salts*	235
	Further Reading		238
10	**The Poroplastic Solid**		**239**
10.1	Basic Concepts of Plasticity		240
	10.1.1	*Plastic loading function and flow rule*	240
	10.1.2	*The principle of maximum plastic work*	242
	10.1.3	*Hardening plasticity*	246
	10.1.4	*Dilatancy*	250
	10.1.5	*Three-dimensional plasticity*	253
	10.1.6	*Limit analysis and stability of dry sandpiles*	254
10.2	From Plasticity to Poroplasticity		256
	10.2.1	*The poroplastic solid*	256

10.1002/9780470710388.fmatter, Downloaded from https://onlinelibrary.wiley.com/doi/10.1002/9780470710388.fmatter by Sandia National Laboratories, Wiley Online Library on [11/09/2025]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

10.2.2 Critical state and the Cam-clay model 260
10.2.3 Capillary hardening and capillary collapse 263
10.2.4 Stability of wet sandpiles 266
10.3 From Material to Structure 267
Further Reading 269

11 By Way of Conclusion **271**
Further Reading 275

Index **277**

10.1002/9780470710388.fmatter, Downloaded from https://onlinelibrary.wiley.com/doi/10.1002/9780470710388.fmatter by Sandia National Laboratories, Wiley Online Library on [11/09/2025]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

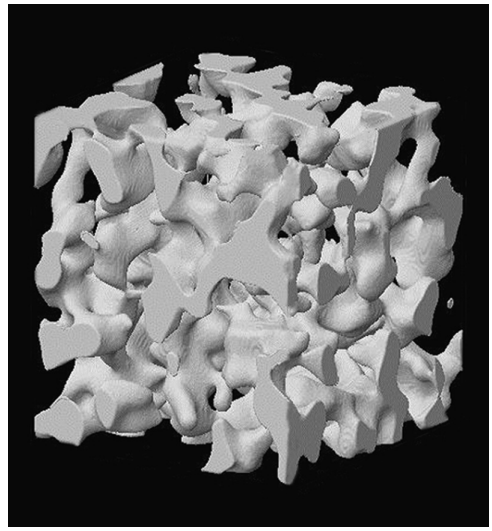

Figure 1 Three dimensional reconstruction of Vycor®glass (courtesy of Pierre Levitz)

10.1002/9780470710388.fmatter, Downloaded from https://onlinelibrary.wiley.com/doi/10.1002/9780470710388.fmatter by Sandia National Laboratories, Wiley Online Library on [11/09/2025]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

Preface

Nowadays it is a nearly impossible task to master all the knowledge required to be innovative in a specialized field, without missing the infinite variety and beauty offered by the many fields of science. In his acceptance talk *Science and the Engineer* for the Timoshenko Award Medal in 1962, Maurice Antony Biot (1905–1985) said that he believed 'that engineers and engineering schools will play an important part in restoring unity and a central viewpoint in the natural sciences. This is because modern engineering, by its very nature, must be synthetic. Specialization, carried to an extreme, is a form of death and decay'.

More than 45 years later the observation of M. A. Biot remains a topical issue. If we do not want to build a Babel Tower of sciences, that will be deserted by the coming generations of students, it becomes more urgent every day to increase the number of interdisciplinary educational programs, which do not focus prematurely on specific disciplines, as well as giving some insights into the history of sciences. As the French philosopher Auguste Comte (1798–1857) said, 'on ne connaît pas complètement une science tant qu'on n'en sait pas l'histoire' (you don't completely know a science if you don't know its history). With this spirit in mind, as well as the modest field that the mechanics and physics of porous solids covers, this book has tried to cross the boundary, from the continuum mechanics of solids, towards the physical chemistry of porous solids. It originates from a course I have been giving for several years as a Professor at Ecole des Ponts ParisTech in the interdisciplinary master of science 'Materials Science for Sustainable Construction'.

When writing this book I have experienced the strength and the accuracy of the celebrated words of the poet John Donne (1572–1631), 'no man is an island'. Indeed, this book has taken advantage of collaborations and discussions with my colleagues and my PhD students covering nearly three decades. Even though some of the results given in this book are due to them, they are too numerous to be named individually. However, I am specially indebted to Sébastien Brisard for his enthusiastic help. He read this book in its early version, commented on it meticulously and suggested many improvements, though any remaining errors are, of course, of my own. I am also pleased to express my gratitude to Matthieu Vandamme, Laurent Brochard and Jean-Michel Pereira for their efficient feedback and perceptive remarks with regard to the topics addressed in this book. The existence of this book would not have been possible without the constant support through the years of my institution, the Laboratoire Central des Ponts et Chaussées.

10.1002/9780470710388.fmatter, Downloaded from https://onlinelibrary.wiley.com/doi/10.1002/9780470710388.fmatter by Sandia National Laboratories, Wiley Online Library on [11/09/2025]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

deformation needs to be described and is conveniently accounted for through the variation of the porosity. Because of the existence of the internal pore pressure applied on the internal walls, the stress tensor $\underline{\underline{\Sigma}}$ is not sufficient to describe the internal forces acting upon the porous solid. As a result the strain work density dW, defined by Equations (3.46) or (3.48), cannot account for the strain work relative to the porous solid only. This section addresses these various issues, by extending the basic concepts of the mechanics of solids to porous solids.

3.4.1 Porosity and deformation

The porosity relative to a volume of porous solid is the fraction of that volume formed from pores. Let n be the porosity of the *current* volume $d\Omega$ of the solid under concern, so that the pores occupy the volume $nd\Omega$ in the current configuration. Because it refers the current volume to the current configuration, n is termed Eulerian porosity. Since the overall volume $d\Omega$ of the solid changes throughout the deformation, the infinitesimal change dn of the Eulerian porosity n does not account for the actual volume change undergone by the porous space. In contrast to the Eulerian porosity n, the volume change of the porous space is accounted for by the change of the Lagrangian porosity φ, which refers the current porous volume to the initial volume $d\Omega_0$ according to

$$\phi\, d\Omega_0 = n\, d\Omega \quad (3.49)$$

The change in the porous space is then given by $(\varphi - \varphi_0)\, d\Omega_0$, where φ_0 stands for the initial Lagrangian porosity. In the following text we will adopt the notation

$$\varphi = \phi - \phi_0 \quad (3.50)$$

The observable macroscopic volume dilation ϵ undergone by the porous solid is due to both the volumetric dilation ϕ/φ_0 of the porous volume to the volumetric dilation ϵ_S undergone by the solid matrix forming the solid part of the porous solid, albeit the latter is not accessible from purely macroscopic experiments. However, in a way similar to Equation (3.17) the very definition of ϵ_S allows us to write

$$d\Omega^S = (1 + \epsilon_S)\, d\Omega_0^S \quad (3.51)$$

where

$$d\Omega^S = (1 - n)\, d\Omega; \quad d\Omega_0^S = (1 - \phi_0)\, d\Omega_0 \quad (3.52)$$

The combination of Equations (3.17) and (3.49)-(3.52) provides the volumetric dilation balance

$$\epsilon = (1 - \phi_0)\,\epsilon_S + \varphi \quad (3.53)$$

where the solid volumetric dilation ϵ_S and the pore volumetric dilation ϕ/φ_0 are weighted by the volume fractions $1 - \varphi_0$ and φ_0, respectively.

The porosity involved later on will always be the connected porosity, that is the porosity relative to the porous space through which the filtration of the saturating fluids can actually occur. In contrast to this connected porosity the porous solid may also contain an occluded porosity, whether saturated or not, but through which no filtration occurs. The deformation of this occluded porosity is included in ϵ_S. When there is no occluded porosity and when, as in the case of soils, the solid part of the porous solid is formed of poorly compressible grains, the solid matrix can be considered as incompressible. This results in $\epsilon_S = 0$ which, substituted in Equation (3.53), leads to

$$\epsilon = \varphi \quad (3.54)$$

Equation (3.54) means that the volumetric dilation ϵ observed at the macroscopic scale results from the deformation of the pore space only.

In soil mechanics the current degree of compactness of a porous material is suitably accounted for by the void ratio e, which is defined as the ratio of the current pore volume to the current volume of

Copyrighted material