

Diffusion and Reactions in Fractals and Disordered Systems

Daniel ben-Avraham

Clarkson University

and

Shlomo Havlin

Bar-Ilan University



CAMBRIDGE
UNIVERSITY PRESS

PUBLISHED BY THE PRESS SYNDICATE OF THE UNIVERSITY OF CAMBRIDGE
The Pitt Building, Trumpington Street, Cambridge, United Kingdom

CAMBRIDGE UNIVERSITY PRESS

The Edinburgh Building, Cambridge CB2 2RU, UK
40 West 20th Street, New York, NY 10011-4211, USA

10 Stamford Road, Oakleigh, VIC 3166, Australia

Ruiz de Alarcón 13, 28014, Madrid, Spain

Dock House, The Waterfront, Cape Town 8001, South Africa

<http://www.cambridge.org>

© Daniel ben-Avraham and Shlomo Havlin 2000

This book is in copyright. Subject to statutory exception
and to the provisions of relevant collective licensing agreements,
no reproduction of any part may take place without
the written permission of Cambridge University Press.

First published 2000

Printed in the United Kingdom at the University Press, Cambridge

Typeface Times 11/14pt. *System* L^AT_EX 2_ε [DBD]

A catalogue record of this book is available from the British Library

Library of Congress Cataloguing in Publication data

Ben-Avraham, Daniel, 1957–

Diffusion and reactions in fractals and disordered systems /

Daniel ben-Avraham and Shlomo Havlin.

p. cm. ISBN 0 521 62278 6 (hc.)

1. Diffusion. 2. Fractals. 3. Stochastic processes. I. Havlin, Shlomo. II. Title.

QC185.B46 2000

530.4'75–dc21 00-023591 CIP

ISBN 0 521 62278 6 hardback

Diffusion and Reactions in Fractals and Disordered Systems

Fractal structures are found everywhere in Nature, and as a consequence anomalous diffusion has far-reaching implications for a host of phenomena. This book describes diffusion and transport in disordered media such as fractals, porous rocks, and random resistor networks. Part I contains material of general interest to statistical physics: fractals, percolation theory, regular random walks and diffusion, continuous-time random walks, and Lévy walks and flights. Part II covers anomalous diffusion in fractals and disordered media, while Part III serves as an introduction to the kinetics of diffusion-limited reactions. Part IV discusses the problem of diffusion-limited coalescence in one dimension. This book written in a pedagogical style is intended for upper-level undergraduates and graduate students studying physics, chemistry, and engineering. It will also be of particular interest to young researchers requiring a clear introduction to the field.

DANIEL BEN-AVRAHAM was born in 1957, in Sante Fe, Argentina, and obtained his Ph.D. in Physics from Bar-Ilan University in 1985. After a 2-year post-doctoral position in the Center of Polymer Studies at the University of Boston, he gained a permanent position at Clarkson University where he is now Associate Professor of Physics. Professor ben-Avraham has spent time as a Visiting Professor at various institutions including Heidelberg University, Bar-Ilan University, and the European Centre for Molecular Biology. He has published over 80 papers and contributed invited papers to several anthologies.

SHLOMO HAVLIN was born in 1942, in Jerusalem, Israel, and obtained his Ph.D. in 1972 from Bar-Ilan University. He stayed at Bar-Ilan University, progressing through the ranks of Research Associate, Lecturer, Senior Lecturer, and Associate Professor until in 1984 he became Professor and Chairman of the Department of Physics. He is now currently Dean of the Faculty of Exact Sciences. Since 1978 Professor Havlin has spent time as a Visiting Professor at numerous institutions including the University of Edinburgh, the National Institute of Health (USA), and Boston University. He is currently on the editorial boards of three journals. He is the author of over 400 papers and editor of ten books. He has given over 40 plenary and invited talks.

to Akiva and Aliza

and

to Hava

Preface

Diffusion in disordered, fractal structures is anomalous, different than that in regular space. Fractal structures are found everywhere in Nature, and as a consequence anomalous diffusion has far-reaching implications for a host of phenomena. We see its effects in flow within fractured and porous rocks, in the anomalous density of states in dilute magnetic systems, in silica aerogels and in glassy ionic conductors, anomalous relaxation in spin glasses and in macromolecules, conductivity of superionic conductors such as hollandite and of percolation clusters of Pb on thin films of Ge and Au, electron-hole recombination in amorphous semiconductors, and fusion and trapping of excitations in porous membrane films, polymeric glasses, and isotropic mixed crystals, to mention a few examples.

It was Pierre Gilles de Gennes who first realized the broad importance of anomalous diffusion, and who coined the term “the ant in the labyrinth”, describing the meandering of random walkers in percolation clusters. Since the pioneering work of de Gennes, the field has expanded very rapidly. The subject has been reviewed by several authors, including ourselves, and from various perspectives. This book builds upon our review on anomalous diffusion from 1987 and it covers the vast material that has accumulated since. Many questions that were unanswered then have been settled, yet, as usual, this has only brought forth a myriad of other questions. Whole new directions of research have emerged, most noticeably in the area of diffusion-limited reactions. The scope of developments is immense and cannot possibly be addressed in one volume. Neither do we have the necessary expertise. Hence, we have chosen once again to base the presentation mostly on heuristic scaling arguments.

The book is written for graduate students, and as an introduction to researchers wishing to enter the field. Much emphasis has been put on its pedagogical value. The end of each chapter includes exercises, open challenges, and references for further reading. The list of open challenges is not exhaustive. It is intended to inspire beginners (many of the challenges require computer programming, for

which our youngsters show remarkable aptitude), and to educate the readers to identify new directions of research. Likewise, the references given are simply those that we had at hand. Many excellent works have been left out. Nothing is implied about their relative priority or importance. We merely wished to convey a general impression of the field's scope, and to provide with some starting points. In spite of our efforts, there are bound to be misprints, inaccuracies, and outright mistakes. Please alert us to their presence by sending messages to benavraham@clarkson.edu (D.b-A.), or to havlin@ophir.ph.biu.ac.il (S.H.).

The book is divided into four parts. Although they are closely related, they can be studied independently from one another. We ourselves have used different combinations in several graduate and upper-level undergraduate courses. Part I contains material of general interest to statistical physics: fractals, percolation theory, regular random walks and diffusion, continuous time random walks, and Lévy walks and flights. Part II expands on our previous review, covering anomalous diffusion in fractals and disordered media. Part III serves as an introduction to the kinetics of diffusion-limited reactions. (The classical case of reaction-limited kinetics is briefly reviewed in Chapter 11.) By and large, the approach used in Parts II and III is that of scaling. Diffusion-limited reactions are still poorly understood, so we believe that examples of exactly solvable models are particularly important. One such example is discussed in Part IV, where we attack the problem of diffusion-limited coalescence in one dimension with the method of inter-particle distribution functions.

We wish to thank our colleagues L. A. N. Amaral, J. S. Andrade, M. Barthelemy, S. Buldyrev, A. Bunde, M. A. Burschka, C. R. Doering, N. V. Dokholyan, A. L. Goldberger, P. Ch. Ivanov, P. R. King, J. Klafter, R. Kopelman, E. Koscielny-Bunde, P. A. Krapivsky, H. Larralde, Y. Lee, F. Leyvraz, R. Nossal, C.-K. Peng, V. Privman, S. Redner, H. E. Roman, S. Russ, M. Schwartz, S. Schwarzer, H. Sompolinsky, H. E. Stanley, H. Taitelbaum, G. M. Viswanathan, I. Webman, and G. Weiss for years of fruitful collaborations, and we gratefully acknowledge the input of our students. Special thanks are due to Jan Kantelhardt for the beautiful cover color prints, to Roi Elran for his help with the preparation of the figures, and to S. Capelin, J. Clegg, S. Holt, and T. Fishlock, of Cambridge University Press, for their patience and for help with the technical aspects of publishing. This book could not have been written without the help of our families and friends. We thank them for their continuous encouragement and support.

Daniel ben-Avraham

Shlomo Havlin

Contents

<i>Preface</i>	<i>page xiii</i>
Part one: Basic concepts	1
1 Fractals	3
1.1 Deterministic fractals	3
1.2 Properties of fractals	6
1.3 Random fractals	7
1.4 Self-affine fractals	9
1.5 Exercises	11
1.6 Open challenges	12
1.7 Further reading	12
2 Percolation	13
2.1 The percolation transition	13
2.2 The fractal dimension of percolation	18
2.3 Structural properties	21
2.4 Percolation on the Cayley tree and scaling	25
2.5 Exercises	28
2.6 Open challenges	30
2.7 Further reading	31
3 Random walks and diffusion	33
3.1 The simple random walk	33
3.2 Probability densities and the method of characteristic functions	35
3.3 The continuum limit: diffusion	37
3.4 Einstein's relation for diffusion and conductivity	39
3.5 Continuous-time random walks	41
3.6 Exercises	43

3.7	Open challenges	44
3.8	Further reading	45
4	Beyond random walks	46
4.1	Random walks as fractal objects	46
4.2	Anomalous continuous-time random walks	47
4.3	Lévy flights and Lévy walks	48
4.4	Long-range correlated walks	50
4.5	One-dimensional walks and landscapes	53
4.6	Exercises	55
4.7	Open challenges	55
4.8	Further reading	56
	Part two: Anomalous diffusion	57
5	Diffusion in the Sierpinski gasket	59
5.1	Anomalous diffusion	59
5.2	The first-passage time	61
5.3	Conductivity and the Einstein relation	63
5.4	The density of states: fractons and the spectral dimension	65
5.5	Probability densities	67
5.6	Exercises	70
5.7	Open challenges	71
5.8	Further reading	72
6	Diffusion in percolation clusters	74
6.1	The analogy with diffusion in fractals	74
6.2	Two ensembles	75
6.3	Scaling analysis	77
6.4	The Alexander–Orbach conjecture	79
6.5	Fractons	82
6.6	The chemical distance metric	83
6.7	Diffusion probability densities	87
6.8	Conductivity and multifractals	89
6.9	Numerical values of dynamical critical exponents	92
6.10	Dynamical exponents in continuum percolation	92
6.11	Exercises	94
6.12	Open challenges	95
6.13	Further reading	96
7	Diffusion in loopless structures	98
7.1	Loopless fractals	98

7.2	The relation between transport and structural exponents	101
7.3	Diffusion in lattice animals	103
7.4	Diffusion in DLAs	104
7.5	Diffusion in combs with infinitely long teeth	106
7.6	Diffusion in combs with varying teeth lengths	108
7.7	Exercises	110
7.8	Open challenges	112
7.9	Further reading	113
8	Disordered transition rates	114
8.1	Types of disorder	114
8.2	The power-law distribution of transition rates	117
8.3	The power-law distribution of potential barriers and wells	118
8.4	Barriers and wells in strips ($n \times \infty$) and in $d \geq 2$	119
8.5	Barriers and wells in fractals	121
8.6	Random transition rates in one dimension	122
8.7	Exercises	124
8.8	Open challenges	125
8.9	Further reading	126
9	Biased anomalous diffusion	127
9.1	Delay in a tooth under bias	128
9.2	Combs with exponential distributions of teeth lengths	129
9.3	Combs with power-law distributions of teeth lengths	131
9.4	Topological bias in percolation clusters	132
9.5	Cartesian bias in percolation clusters	133
9.6	Bias along the backbone	135
9.7	Time-dependent bias	136
9.8	Exercises	138
9.9	Open challenges	139
9.10	Further reading	140
10	Excluded-volume interactions	141
10.1	Tracer diffusion	141
10.2	Tracer diffusion in fractals	143
10.3	Self-avoiding walks	144
10.4	Flory's theory	146
10.5	SAWs in fractals	148
10.6	Exercises	151
10.7	Open challenges	152
10.8	Further reading	153

Part three: Diffusion-limited reactions	155
11 Classical models of reactions	157
11.1 The limiting behavior of reaction processes	157
11.2 Classical rate equations	159
11.3 Kinetic phase transitions	161
11.4 Reaction–diffusion equations	163
11.5 Exercises	164
11.6 Open challenges	166
11.7 Further reading	166
12 Trapping	167
12.1 Smoluchowski's model and the trapping problem	167
12.2 Long-time survival probabilities	168
12.3 The distance to the nearest surviving particle	171
12.4 Mobile traps	174
12.5 Imperfect traps	174
12.6 Exercises	175
12.7 Open challenges	176
12.8 Further reading	177
13 Simple reaction models	179
13.1 One-species reactions: scaling and effective rate equations	179
13.2 Two-species annihilation: segregation	182
13.3 Discrete fluctuations	185
13.4 Other models	187
13.5 Exercises	189
13.6 Open challenges	189
13.7 Further reading	190
14 Reaction–diffusion fronts	192
14.1 The mean-field description	192
14.2 The shape of the reaction front in the mean-field approach	194
14.3 Studies of the front in one dimension	195
14.4 Reaction rates in percolation	196
14.5 $A + B_{\text{static}} \rightarrow C$ with a localized source of A particles	200
14.6 Exercises	201
14.7 Open challenges	202
14.8 Further reading	203

Part four: Diffusion-limited coalescence: an exactly solvable model	205
15 Coalescence and the IPDF method	207
15.1 The one-species coalescence model	207
15.2 The IPDF method	208
15.3 The continuum limit	211
15.4 Exact evolution equations	212
15.5 The general solution	213
15.6 Exercises	215
15.7 Open challenges	216
15.8 Further reading	216
16 Irreversible coalescence	217
16.1 Simple coalescence, $A + A \rightarrow A$	217
16.2 Coalescence with input	222
16.3 Rate equations	223
16.4 Exercises	227
16.5 Open challenges	228
16.6 Further reading	228
17 Reversible coalescence	229
17.1 The equilibrium steady state	229
17.2 The approach to equilibrium: a dynamical phase transition	231
17.3 Rate equations	233
17.4 Finite-size effects	234
17.5 Exercises	236
17.6 Open challenges	237
17.7 Further reading	237
18 Complete representations of coalescence	238
18.1 Inhomogeneous initial conditions	238
18.2 Fisher waves	240
18.3 Multiple-point correlation functions	243
18.4 Shielding	245
18.5 Exercises	247
18.6 Open challenges	247
18.7 Further reading	248
19 Finite reaction rates	249
19.1 A model for finite coalescence rates	249
19.2 The approximation method	250
19.3 Kinetics crossover	251
19.4 Finite-rate coalescence with input	254

19.5 Exercises	256
19.6 Open challenges	257
19.7 Further reading	257
<i>Appendix A The fractal dimension</i>	258
<i>Appendix B The number of distinct sites visited by random walks</i>	260
<i>Appendix C Exact enumeration</i>	263
<i>Appendix D Long-range correlations</i>	266
<i>References</i>	272
<i>Index</i>	313

Part one

Basic concepts

The first part of the book includes introductory concepts and background necessary for the understanding of anomalous diffusion in disordered media.

Fractals might be familiar to most readers, but their importance in modeling disordered and random media, as well as certain characteristics of the trails made by diffusing particles, makes it worthwhile to spend some time reviewing the subject. In Chapter 1 we provide working definitions of fractals, fractal dimensions, self-affine fractals, and related ideas. More importantly, we describe several algorithms for determining whether a particular object is a fractal, and for finding its fractal dimension. In the early days of fractal theory much effort was spent on merely exploring the fractal properties of various natural objects and physical models, using precisely such algorithms, and they continue to be essential tools for the study of disordered phenomena.

Percolation, which is reviewed in Chapter 2, is perhaps the most important model of disordered media and of naturally occurring fractals. Percolation owes its enormous appeal to its simplicity (it can be defined and analyzed using only geometrical concepts), its remarkably wide range of applications, and its being one of the most basic models of critical phase transitions. Relevant to our purpose is the fact that studies of anomalous diffusion have traditionally focused on percolation systems, and the problem still attracts considerable interest. The percolation transition, on the other hand, gives us an excellent opportunity to introduce several useful concepts, such as critical exponents, scaling, and the upper critical dimension.

In Chapter 3 we present a brief introduction to random-walk theory. Discrete random walks (in regular lattices) are discussed first, then diffusion and the diffusion equation are obtained as limiting cases. In the course of the book, we shift freely between these discrete (random walk) and continuous (diffusion)

representations. The method of generating functions is discussed in some detail, owing to its wide applicability in other realms of statistical physics. It also eases the introduction and discussion of continuous-time random walks (CTRWs).

Finally, in Chapter 4 we review other popular models of transport: Lévy walks, Lévy flights, and long-range correlated walks. These (and some instances of the CTRW) were originally introduced as models that exhibit anomalous transport kinetics even in *regular* lattices, and are therefore relatively easy to analyze, but eventually they came to be studied also in fractals and disordered lattices.

1

Fractals

Fractals model disorder in Nature far more successfully than do objects of classical geometry. In the now famous words of B. Mandelbrot: “Clouds are not spheres, mountains are not cones, coastlines are not circles, bark is not smooth, nor does lightning travel in a straight line” (Mandelbrot, 1982). We begin with a discussion of fractals and their most basic properties: self-similarity and symmetry under dilation, or scaling, and the fractal dimension and the ways to determine it. Our goal is to develop an intuitive understanding, and to provide some basic working tools.

1.1 Deterministic fractals

Deterministic fractals are idealized geometrical structures with the property that parts of the structure are similar to the whole. While this self-similarity is a general property of fractals, it is rather a vague definition, and the best way to understand what fractals really are is through examples. Some well-known deterministic fractals are shown in Figs. 1.1–1.3.

The Koch curve (Fig. 1.1) is constructed from a unit segment. The middle third section is replaced by two other segments of length $\frac{1}{3}$, making a tent shape, as seen in Fig. 1.1a. The same procedure is repeated for each of the four resulting segments (of length $\frac{1}{3}$). This process is iterated *ad infinitum*. The limiting curve is of infinite length, yet it is confined to a finite region of the plane. Thus, the Koch curve is somewhat “denser” than a regular curve of dimension $d = 1$, but certainly “sparser” than a two-dimensional object (its area is zero!). Intuitively, then, its dimension should be between one and two. If a regular object – such as a line segment, a square, or a cube, etc. – of dimension d is magnified by a factor b , the original object would fit b^d times in the magnified one. This consideration may serve as a working definition of the *fractal dimension*, d_f (see Appendix A for more rigorous definitions). In the Koch curve, magnified by a factor of three, there

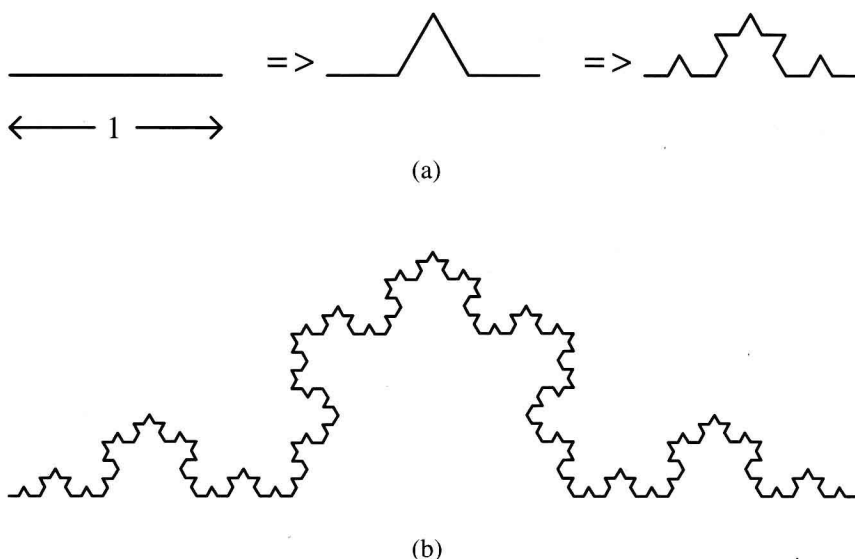


Fig. 1.1. The Koch curve. (a) Construction of the curve. The initiator is a unit segment. The generator replaces the middle third section by two similar sections, forming the shape of a tent. Two iterations of this process are shown. (b) The Koch curve after four iterations.

fit exactly four of the original curves. Therefore, its fractal dimension is given by $3^{d_f} = 4$, or $d_f = \ln 4 / \ln 3 \simeq 1.262$.

Perhaps the most popular fractal is the Sierpinski gasket (Fig. 1.2). Here one begins with an equilateral triangle that is divided into four equal subunits, and the central subunit is discarded. Again, the process is repeated recursively. The resulting fractal dimension is given by $2^{d_f} = 3$, or $d_f = \ln 3 / \ln 2 \simeq 1.585$.

The Sierpinski sponge (also known as the Menger sponge) (Fig. 1.3) is generated from a cube that is subdivided into $3 \times 3 \times 3 = 27$ smaller cubes. The small cube at the center and its six nearest neighbors are then discarded. The same is done with each of the remaining 20 cubes, and the process is iterated indefinitely. The limiting object has *zero* volume, but *infinite* surface area. This property is consistent with the fractal dimension of the sponge; $3^{d_f} = 20$, or $d_f = \ln 20 / \ln 3 \simeq 2.727$, between two and three.

All deterministic fractal lattices are obtained in a similar way to the examples above. Construction begins from a genus, called the *initiator* (e.g., the unit segment in the case of the Koch curve, an equilateral triangle for the Sierpinski gasket, etc.) and proceeds with a set of operations that are repeated indefinitely in a recursive fashion. This set of operations is called the *generator*.

The generator may be one of two kinds. In one case, the initiator is replaced by *smaller* replicas of itself and the fractal builds inwardly, towards ever smaller