Diffusion and Reactions in Fractals and Disordered Systems

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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.

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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.

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Daniel ben-Avraham

Shlomo Havlin

Contents

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.

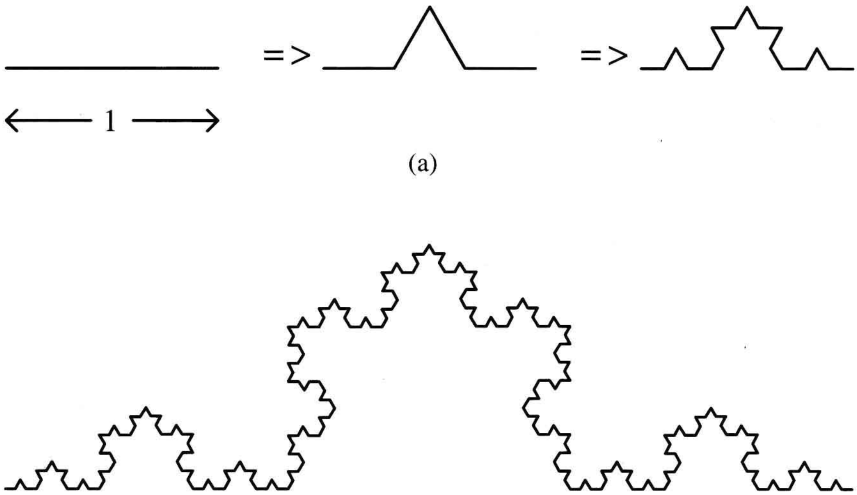
1
Fractals

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



(a)

(b)

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 $3^{d_\mathrm{f}} = 4$, or $d_\mathrm{f} = \ln 4/\ln 3 \simeq 1.262$.

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 $2^{d_\mathrm{f}} = 3$, or $d_\mathrm{f} = \ln 3/\ln 2 \simeq 1.585$.

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; $3^{d_\mathrm{f}} = 20$, or $d_\mathrm{f} = \ln 20/\ln 3 \simeq 2.727$, 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