MOLECULES, DYNAMICS MILITARY MILI

AN INTRODUCTION TO SELF-ORGANIZATION OF MATTER

A. BABLOYANTZ

Volume IV in the Wiley Series in Nonequilibrium Problems in the Physical Sciences and Biology Series Editors: I. Prigogine and G. Nicolis

MOLECULES, DYNAMICS, AND LIFE

An Introduction to Self-Organization of Matter

A. BABLOYANTZ

University of Brussels Brussels, Belgium

A WILEY-INTERSCIENCE PUBLICATION

JOHN WILEY & SONS

New York · Chichester · Brisbane · Toronto · Singapore

To Eric and Michel

Copyright © 1986 by John Wiley & Sons, Inc.

All rights reserved. Published simultaneously in Canada.

Reproduction or translation of any part of this work beyond that permitted by Section 107 or 108 of the 1976 United States Copyright Act without the permission of the copyright owner is unlawful. Requests for permission or further information should be addressed to the Permission Department, John Wiley & Sons, Inc.

Library of Congress Cataloging in Publication Data:

Babloyantz, A. (Agnessa)

Molecules, dynamics, and life.

(Nonequilibrium problems in the physical sciences and biology, ISSN 0275-9292; v. 4)

"A Wiley-Interscience publication."

Bibliography: p. Includes index.

- 1. Molecular biology. 2. Thermodynamics.
- 3. Biophysics. I. Title. II. Series.

QH506.B33 1986

574.8'8 85-26413

ISBN 0-471-82380-5

Printed in the United States of America

10987654321

MOLECULES, DYNAMICS, AND LIFE

NONEQUILIBRIUM PROBLEMS IN THE PHYSICAL SCIENCES AND BIOLOGY

Editors: I. Prigogine and G. Nicolis Université Libre de Bruxelles Brussels, Belgium

Volume 1: G. NICOLIS, G. DEWEL, AND J. W. TURNER, Order and Fluctuations in Equilibrium and Nonequilibrium Statistical Mechanics: XVIIth International Solvay Conference on Physics

Volume II: C. W. HORTON, L. E. REICHL, AND V. G. SZEBEHELY Long-Time Prediction in Dynamics

Volume III: G. W. HORTON, JR. AND L. E. REICHL Statistical Physics and Chaos in Fusion Plasmas

Volume IV: A. BABLOYANTZ

Molecules, Dynamics, and Life: An Introduction to Self-Organization of Matter

FOREWORD

It is now nearly 40 years since I published a monograph, Etude thermodynamique des phénomènes irréversibles (See Chapter 4), devoted specifically to thermodynamics of nonequilibrium and self-organization.

This was a slim book. Very little was known outside equilibrium state. Today, the intellectual landscape has undergone drastic changes. A fundamental reconceptualization of science is going on. We have long known that we are living in a pluralistic world in which we find deterministic as well as stochastic phenomena, reversible as well as irreversible. We observe deterministic phenomena such as the frictionless pendulum or the trajectory of the moon around the earth; moreover, we know that the frictionless pendulum is also reversible, as future and past play the same role in the equations describing the motion of the pendulum. But other processes, such as diffusion or chemical reactions, are irreversible. Here, there is a privileged direction of time: the system becomes uniform after some time. We must also acknowledge the existence of stochastic processes if we want to avoid the paradox of referring to the variety of natural phenomena as a blueprint designed at the very moment of the Big Bang.

What has changed since the beginning of this century is our evaluation of the relative importance of these types of phenomena.

The artificial may be deterministic and reversible. The natural contains essential elements of randomness and irreversibility.

At the start of this century, continuing the tradition of the classical approach, physicists were almost unanimous in admitting that the fundamental laws of the universe were deterministic and reversible. Processes which did not fit this scheme were supposed to be exceptions, mere artifacts of some apparent complexity, which itself had to be accounted for by invoking our ignorance, or lack of control over the variables involved. Now that we are at the end of this century, we are more and more inclined to think that the fundamental laws of nature are irreversible and stochastic; that deterministic and reversible laws are applicable only in limited situations.

This change in our outlook on the world has been the subject of numerous monographs and review articles. However, the emphasis is generally put on the formal part of the theory, closely related to the advances in our understanding of unstable and nonlinear dynamic systems. This fact clearly

٧

vi Foreword

makes these books difficult to read for most members of the scientific community.

I am therefore very happy to present this book by Agnessa Babloyantz, in which the emphasis is more on the physical content than on the formal aspects of this new outlook. I believe we have to thank Babloyantz for having written a highly readable text, accessible to everyone who is interested in the natural sciences.

As a result of the new ideas developed in the field of nonequilibrium systems, the gap between subjects which were traditionally considered to be "simple" and the ones—such as biology or human sciences—which were thought of as complex is becoming narrower. This leads to the possibility of the transfer of knowledge from one field to another. For this very reason, the present book should be of interest to researchers in fields such as physics, chemistry, biology, and social sciences.

Agnessa Babloyantz is highly qualified to write this book: she has published valuable work devoted to nonequilibrium systems in biology, including significant contributions to morphogenesis, and more recently to the dynamical approach of neural activity, including a study of the fractal geometry of attractors in brain dynamics.

Her recent work has shown that the electrical activity of the brain in deep sleep as monitored by electroencephalogram (EEG) may be modeled by a "fractal attractor." This is remarkable as it shows that the brain acts as a system possessing intrinsic complexity and unpredictability. It is this instability which likely permits the amplification of inputs due to sensory impressions in the waking state.

In spite of the spectacular progress made these last years in nonequilibrium physics and mathematics, in spite of the innumerable conference proceedings and papers which are being published, we are only at the beginning of a new dialog with nature. It may be hoped that this book by Agnessa Babloyantz will be a reliable guide to help students and research workers find their way in this new area.

I. PRIGOGINE

PREFACE

This book sets out to tell the story of how inert matter can acquire selforganizing and other properties usually ascribed to life. There are many excellent popular books in the various fields of science which present to the reader all the magic of knowledge in the manner of an exciting thriller. The reader is not invited behind the scenes but is only shown the finished results, which might have taken a few days or a few centuries to realize.

The next stage in scientific writing is the elementary textbook. In such books the author chooses a well-defined subject and guides the reader through the topic. Step by step the reader discovers the methods, the logic, the rigor, and also the pitfalls and limitations of a particular scientific endeavor. Such textbooks usually require some initial background, a substantial amount of time, and a great deal of motivation.

In this book I try a middle of the road approach, halfway between a popular work and a textbook. As in popular works, the reader is not required to have a solid background in any of the subjects which are discussed. Every scientific concept is explained in common words. The textbook model is reflected in the systematic approach to each subject. Since the book is conceived as a self-sufficient entity, a special effort has been made to incorporate all the necessary information required for an understanding of its main concepts: the self-organization of matter and its relation to living organisms.

The reader is invited behind the scenes, introduced to the kind of questions asked in a scientific endeavor, and shown how answers are found to those questions. Using logic, a scientist accumulates experimental results, generalizes findings into laws, and predicts the future from the present. Whenever possible, I invite the reader to participate in this scientific process. As in a textbook the reader is shown how to solve simple problems. For more complex situations, only the final results are given and are discussed in plain language. Historical facts, dates, and the names of well-known scientists are incorporated into the main body of the narrative, to give some idea of the historical development of the main concepts.

This book is intended for students interested in natural science. It may also interest physicists, chemists, biologists, engineers, and those who desire to learn without too much effort what has happened in their field since they left

viii Preface

college. The reader must have some elementary notions of algebra, and must be familiar with the concepts of differentials, integrals, and differential equations.

This book is composed of three parts, which are connected by the logic of the concept of self-organization.

The first chapter of Part I begins with a few words on the history of the evolution of our ideas concerning matter. It continues with a summary of our present concept of the atom, its internal structure, and the reasons for the association of atoms into molecular assemblies. The details of molecular encounters in the course of a reaction and the amount of change of substances that appear or disappear per second are crucial for the understanding of the self-organizational processes presented in the remaining chapters of the book. Therefore, a relatively large amount of space is devoted to the field of chemical kinetics, which is treated in some detail in Chapter 2. I show how the rate of a chemical reaction may be evaluated. Various elementary reactions are defined; and I indicate how they can be described and studied by mathematical tools.

The concept of entropy and the law which governs its evolution toward a maximum value is the second law of a branch of macroscopic physics called thermodynamics. The development of thermodynamics was triggered by the invention of heat engines. Later, it appeared that thermodynamic methods could be used with great profit for the study of bulk matter, particularly chemical and biochemical processes. In some of their aspects a human body and a machine obey the same laws. Thermodynamic methods are one of the most natural tools for the investigation of macroscopic systems since they are based on the observable and tangible properties of bulk matter. To single out clearly the recent important developments in the field of thermodynamics, the subject is divided quite unusually into four separate parts, which are presented in Chapters 3 to 6 of Part I.

In Chapter 3 I define the important concepts of equilibrium thermodynamics and introduce its four laws. It is shown that the thermodynamics of quiescent systems can be extended to the domain of chemical and biochemical reactions, and therefore to the study of living organisms.

In Chapters 4, 5, and 6 the thermodynamic formalism is extended to irreversible processes. In Chapters 3 and 4 thermodynamic methods are used for the study of the measurable properties of bulk matter. For example, one may evaluate the quantity of energy (calories) contained in a sugar cube or measure the speed with which matter crosses cell walls.

Thermodynamic methods also have predictive value. They indicate the direction of evolution of processes. For example, the evolutionary laws of thermodynamics have convinced scientists once and for all that one cannot design airplanes that can fly with the energy of the ambient air as their unique

source of power, or run a boat with power extracted solely from ocean waters.

Thermodynamics may be used in a third way. With the help of its methods one can test the stability of a given state of matter under given external conditions. Thermodynamic stability criteria tell us what may happen if small disturbances are introduced either by internal fluctuations or by external perturbations in the state of matter.

The recent advances in the theory of thermodynamics of irreversible processes achieved by P. Glansdorff and I. Prigogine have been primarily in the area of the evolution and stability of irreversible processes. In particular, the development of stability criteria for open systems gives the conditions under which the matter can self-organize spontaneously into temporal and spatial structures.

These chapters devoted to thermodynamics stand as a separate entity and may be read independently from the remainder of the book. They will be of special value to engineers and physicists interested in new developments in this field.

Once the self-organization of matter became compatible with the macroscopic laws of physics, researchers were sufficiently motivated to try alternative, nonthermodynamic methods for the study of the behavior of such systems. Kinetic methods for the investigation of dissipative structures are developed in Part II. The reader not particularly keen on thermodynamic concepts and only interested in acquiring a working knowledge of self-organizing systems may omit the discussion of thermodynamic theory and proceed to Part II.

In Part II, Chapter 7 starts with a survey of self-organizational phenomena in various areas of the natural sciences. It shows how extremely diverse and seemingly unrelated phenomena turned out to be governed by a few common principles. Open, nonlinear, and cooperative systems may give rise to self-organized dissipative structures.

The Belousov-Zhabotinski reaction, taken as a prototype of a dissipative structure, is studied in Chapter 8. The origin of oscillations, wave propagation and stationary structures, chaotic behavior, and many other strange properties of this reaction are shown. These unexpected properties open new fields in chemical sciences, and make it possible for us to speak of a "new chemistry."

In Chapter 9 we describe the self-organizational phenomena in terms of a theoretical approach. Methods are given whereby one can easily detect the presence of dissipative structures in chemical reactions. Model reactions are constructed and their time evolution is followed with the help of differential equations and their solutions.

Today the role of self-organization and dissipative structures in the study of living matter is widely recognized. These concepts have entered the fields of

physics, chemistry, biology, population dynamics, and even the social sciences, and have created a multidisciplinary field of research.

To give a comprehensive idea of all the important advances accomplished in the field of self-organized systems would require several volumes. The choice of illustrative examples has not been easy. However, to justify the title of the book, examples had to be taken from the biological sciences. The following criteria were used for selection. Each example illustrates one particular aspect of a living organism that can be traced to one of the self-organizational properties of chemical dissipative structures. All the reported models are studied with the mathematical tools developed in Part II. Finally, many of the examples have been developed by the Brussels school where the new advances in thermodynamics and the ensuing concepts of dissipative structures were developed.

All the examples treated in Part III use mathematical language. The reader is not required to possess a background in biochemistry; all the concepts needed to understand a particular example are furnished in the relevant sections.

Part III begins with a short summary of the evolution of our ideas concerning living organisms, and continues with an account of the structural aspect of important present-day biological macromolecules, indicating how these evolved from simple molecules. With M. Eigen we follow the Darwinian-type evolution of these molecules into hypercycles. These complex and structured entities, following a compartmentalization process, probably gave rise to the first primitive living protocells.

The example treated in Chapter 11 shows how glucose consumption by unicellular yeast cells follows the path of a biochemical clock. We also see how protein synthesis in another unicellular organism follows an all-or-none path characteristic of a dissipative structure.

In Chapter 12 the communication processes among the individuals in a colony of slime molds are shown to be another example of the self-organization of a biochemical medium. Messenger molecules in pacemaker cells spontaneously organize themselves into a collective mode of behavior and are delivered to the other members of the colony in a pulsating fashion.

The example in Chapter 13 deals with the physico-chemical laws which make it possible to generate complete and complex organisms, with many different cellular types, from a single fertilized egg. It is shown that the information for cell differentiation, in the form of a molecular gradient, is generated as a result of self-organizational processes inside the embryo. As the embryo grows, successive self-organized patterns arise and determine the shape and function of the organism.

Adult organisms themselves are the loci of many self-organizational processes. Circadian (diurnal) rhythms and regular heartbeats are two such

processes. The brains of higher animals, particularly man, are certainly the ultimate in the self-organization of matter. Our thoughts, feelings, and actions result from the cooperative behavior of the ensemble of a few billion nerve cells. The modeling of an ensemble of intricately interconnected nerve cells raises new technical problems in the mathematical description of dissipative structures. In Chapter 14 these problems are illustrated by the example of the epileptic seizure, which is a pathological state of brain activity.

The general subject of the self-organization of matter has been treated in several books at various levels of complexity. Thermodynamics of Structure, Stability, and Fluctuations by P. Glansdorff and I. Prigogine, and Self-organization in Nonequilibrium Systems by G. Nicolis and I. Prigogine are advanced works. Both address themselves to researchers in the field. From Being to Becoming by I. Prigogine is at an intermediary level, whereas Order Out of Chaos, by the same author and I. Stengers, addresses the philosophical implications of self-organizing systems.

The Hypercycle by M. Eigen and P. Schuster and Laws of the Game by M. Eigen and R. Winkler are more oriented toward self-organizational problems in relation to the emergence of the genetic code. In Advanced Synergetics, H. Haken is more concerned with physical systems. He is especially interested in the origin of laser beams. Interested readers may find more specialized books referred to in the various chapters of the present work.

This book attempts to expound scientific processes which took innumerable research workers several centuries to discover. It is impossible to refer to all of those workers. I have chosen only to occasionally cite some famous names which probably are familiar to some readers. In the description of contemporary material I mention only researchers whose work has been used in the book.

Brussels, Belgium January 1986 A. BABLOYANTZ

ACKNOWLEDGMENTS

My encounter with Professor I. Prigogine has been the turning point in my life. During more than two decades he has advised and guided me through the pathways of the theoretical study of nature. Starting from the study of the relatively simple hydrogen molecule, he has made me bifurcate by successive transitions into more and more complex areas of research. With his broad view of science and the humanities he has been a constant source of innovation and enthusiasm. I wish to thank him for his teaching, for making this book possible, and for his unwavering support on bad as well as good days.

My very special gratitude goes to Professor P. Glansdorff for spending so much of his time in reading and criticizing the manuscript. I have benefited greatly from his vast knowledge of thermodynamics and his precise mind in the preparation of the first part of this book.

I am also grateful to my friend and colleague Professor G. Nicolis for his constant support, helpful discussions, and his reading of the manuscript. His advice and encouragement have been invaluable not only for the preparation of this book but throughout my entire career.

The multidisciplinary nature of this book reflects the diversity of the subjects studied by friends and colleagues at the University of Brussels and the University of Texas in Austin. I wish to thank particularly P. Allen, P. Borckmans, K. Chemla, J. L. Deneubourg, G. Dewel, T. Erneux, C. George, A. Goldbeter, M. Herschkowitz-Kaufman, J. Hiernaux, L. Kaczmarek, D. Kondepudi, R. Lefever, M. Malek-Mansour, F. Mayne, A. Nazarea, C. Nicolis, S. Pahaut, M. Sanglier, A. Sanfeld-Steinchen, J. W. Turner, and D. Walgraef.

I am grateful to Professors B. Baranowski of the University of Warsaw, R. Mazo of the University of Oregon, R. Hansell of the University of Toronto, and V. Mathot, E. Vander Donckt and J. C. Legros of the University of Brussels for their criticisms of the manuscript.

It is a pleasure to thank C. Brian, J. McGill, and D. Newson for their help with English style.

The preparation of the manuscript was made possible with the efficient

xiv Acknowledgments

assistance of S. Dereumaux-Wellens, D. Hanquet, N. Sardo, and M. Adam. I thank them for their help.

I wish to express my especial gratitude to my friend P. Kinet, whose technical skill in preparing the illustrations for this book was invaluable.

A. B.

CONTENTS

Introduction 1				
PAI	RT I.	MATTER AND CHEMISTRY		
1.	The S	Structure of Matter	9	
	1.1 1.2 1.3 1.4 1.5 1.6	Quantum Mechanics 18 Chemical Bonds 20 Chemical Reactions 22		
2.	Chemi	ical Kinetics	25	
	2.1 2.2 2.3 2.4 2.5 2.6	Rates: Definitions 27 Experimental Measurement of Rates 27		
		Reversible Reactions 32 Determination of Rate Constants 33		

3.	Equilib	orium Thermodynamics	39
	3.1 3.2 3.3 3.4 3.5 3.6	Why Thermodynamics? 39 The Science of Fire 40 A Thermodynamic System: Definitions 42 Equilibrium Thermodynamics 44 The Zero Law and the Concept of Temperature 45 The First Law of Thermodynamics 46	
	5.0	3.6.1 Measurement of Internal Energy 48 3.6.2 Internal Energy Function 50	
	3.7	The Second Law of Thermodynamics 51 3.7.1 Reversible Processes 51 3.7.2 Irreversible Processes 52 3.7.3 The Birth of the Second Law 53 3.7.4 The Entropy of an Ideal Gas 56 3.7.5 Direction of Change of Entropy 58 3.7.6 Why Does a Cup of Coffee Get Cold? 59	
	3.8	The Third Law of Thermodynamics 60	
	3.9	How to Use the Thermodynamic Formalism 60	
	3.10	The Generalized Thermodynamic Formalism 61 3.10.1 Composition as a New Variable 62 3.10.2 Open Systems 63 3.10.3 Other Thermodynamic Potentials 64 3.10.4 Physical Interpretation of Thermodynamic Potentials 64 3.10.5 Molar Quantities 66 Chemical Thermodynamics 68	
	3.11		
		 3.11.2 Affinity and Progress of a Chemical Reaction 70 3.11.3 Why Does the Smell of Perfume Diffuse? 72 3.11.4 Equilibrium Constant and Heat of Reaction 73 	
	3.12	The Limits of Equilibrium Thermodynamics 75	
4.	Noneq	quilibrium Thermodynamics	77
	4.1 4.2 4.3 4.4	Introduction 77 Irreversible Processes 78 Entropy of a Nonequilibrium System 79 Entropy Production 80 4.4.1 Change in Time of a Conserved Quantity 81 4.4.2 Change in Time of Local Internal Energy 82	
		4.4.3 Change in Time of Local Entropy 83	

Contents	xvi

4.5 4.6 4.7 4.8 4.9 4.10 4.11 4.12	Linear Thermodynamics of Irreversible Processes The Onsager Reciprocal Relations 88 Thermal Diffusion 90 The Curie-Prigogine Symmetry Law 94 Diffusion 96 Discontinuous Systems: Thermal Osmosis 97 Biological Membranes 101 The Various Domains of Thermodynamics 104				
5 Evolutionary Criteria					
5.1 5.2	Introduction 107 Evolutionary Criteria for Equilibrium States 107 5.2.1 The Impossibility of Making a Magic Boat 108 5.2.2 A Real Boat 109				
5.3	The Evolutionary Criterion for Nonequilibrium Systems—Linear Domain 111				
5.4	5.3.1 Theorem of Minimum Entropy Production 111 The Evolutionary Criterion for Steady States Far from Equilibrium 113				
6. Stability Criteria					
6.1 6.2 6.3 6.4 6.5 6.6 6.7	Introduction 117 Stability of Equilibrium States 118 Stability of Steady States—Linear Domain 120 Stability of Steady States—Nonlinear Domain 122 Benard or Convective Instability 127 Taylor Instability 129 Instability in a Chemical Reaction 131 Order and Entropy 133				
Conclusion to Part I					
PART II.	A NEW CHEMISTRY				
Introduction	Introduction to Part II				
7. The B	7. The Birth of the New Chemistry				
7.1 7.2	Introduction 141 Chemical Oscillations 141				