Dynamics of
Self-Organized
and Self-Assembled
Structures

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Physical and biological systems driven out of equilibrium may spontaneously evolve to form spatial structures. In some systems molecular constituents may self-assemble to produce complex ordered structures. This book describes how such pattern formation processes occur and how they can be modeled.

Experimental observations are used to introduce the diverse systems and phenomena leading to pattern formation. The physical origins of various spatial structures are discussed, and models for their formation are constructed. In contrast to many treatments, pattern-forming processes in nonequilibrium systems are treated in a coherent fashion. The book shows how near-equilibrium and far-from-equilibrium modeling concepts are often combined to describe physical systems.

This interdisciplinary book can form the basis of graduate courses in pattern formation and self-assembly. It is a useful reference for graduate students and researchers in a number of disciplines, including condensed matter science, nonequilibrium statistical mechanics, nonlinear dynamics, chemical biophysics, materials science, and engineering.

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To our families

The dimmed outlines of phenomenal things all merge into one another unless we put on the focusing glass of theory, and screw it up sometimes to one pitch of definition and sometimes to another, so as to see down into different depths through the great millstone of the world.

Analogies, James Clerk Maxwell

Preface

The idea for this book arose from the observation that similar-looking patterns occur in widely different systems under a variety of conditions. In many cases the patterns are familiar and have been studied for many years. This is true for phase-segregating mixtures where domains of two phases form and coarsen in time. A large spectrum of liquid crystal phases is known to arise from the organization of rod-like molecules to form spatial patterns. The self-assembly of molecular groups into complex structures is the basis for many of the developments in nano-material technology. If systems are studied in far-from-equilibrium conditions, in addition to spatial structures that are similar to those in equilibrium systems, new structures with distinctive properties are seen. Since systems driven out of equilibrium by flows of matter or energy are commonly encountered in nature, the study of these systems takes on added importance. Many biological systems fall into this far-from-equilibrium category.

In an attempt to understand physical phenomena or design materials with new properties, researchers often combine elements from the descriptions of equilibrium and nonequilibrium systems. Typically, pattern formation in equilibrium systems is studied through evolution equations that involve a free energy functional. In far-from-equilibrium conditions such a description is often not possible. However, amplitude equations for the time evolution of the slow modes of the system play the role that free-energy-based equations take in equilibrium systems. Many systems can be modeled by utilizing both equilibrium and nonequilibrium concepts.

Currently, a wide variety of methods is being used to analyze self-organization and self-assembly. In particular, microscopic and mesoscopic approaches are being developed to study complex self-assembly in considerable detail. On mesoscales, fluctuations are important and influence the self-organization one sees on small scales, such as in the living cell. Nevertheless, many common aspects of these pattern-forming processes can be modeled in terms of order parameter fields, which describe the dynamics of relevant collective variables of the system. The patterns

that are formed and the way they evolve are often controlled by certain common elements that include the presence of interfaces, interfacial curvature, and defects.

In order to present an approach to the study of such self-assembled or self-organized structures that highlights common features, we have intentionally limited the scope of the presentation to descriptions based on equations for order parameter fields. Approaches of this type are able to capture the gross features of pattern formation processes in diverse systems, including those in the equilibrium and far-from-equilibrium domains. We have also intentionally omitted descriptions based on various coarse-gained molecular dynamics methods and a variety of other mesoscopic particle-based methods, which are proving to be powerful tools for the study of such systems. In addition, to sharply focus our presentation we have restricted our discussion to systems where hydrodynamic flows are not important.

A selection of the material in this book formed the basis for a one-semester course entitled "Interface Dynamics and Pattern Formation in Nonequilibrium Systems" given jointly in the Departments of Chemistry and Physics at the University of Toronto. Many of the topics covered in the book have been the subjects of intense investigations, and a large literature exists. In order to make the material as self-contained as possible, in most cases we have provided an introduction to each topic in a form that allows the main ideas to be exposed and derived from basic principles. The final chapters of the book provide some additional examples of applications that combine the two underlying themes that are developed in the book: free-energy-functional and amplitude-equation descriptions. These chapters show how the dynamics of physical and biological systems can be modeled using the concepts developed in the body of the book.

Some of the material presented in the book derives from work with our colleagues and students. In particular we would like to acknowledge the contributions of Augustí Careta, Hugues Chaté, Francisco Chávez, Mario Cosenza, Jörn Davidsen, Ken Elder, Simon Fraser, Leon Glass, Martin Grant, Andrew Goryachev, Daniel Gruner, Christopher Hemming, Zhi-Feng Huang, Anna Lawniczak, François Léonard, Roberto Livi, Anatoly Malevanets, Paul Masiar, Alexander Mikhailov, Gian-Luca Oppo, Antonio Politi, Sanjay Puri, Tim Rogers, Katrin Rohlf, Chris Roland, Guillaume Rousseau, Celeste Sagui, Ken Showalter, Kay Tucci, Mikhail Velikanov, Xiao-Guang Wu, Chuck Yeung, and Meng Zhan. We also owe a special debt of gratitude to our colleagues who read and commented on portions of the book: Markus Bär, Jörn Davidsen, Walter Goldburg, Jim Gunton, Christopher Hemming, Zhi-Feng Huang, Chuck Knobler, Maureen Kapral, Alexander Mikhailov, Steve Morris, Evelyn Sander, Len Sander, Celeste Sagui, Peter Voorhees, Tom Wanner, Chuck Yeung, and Royce Zia. The preparation of this book would have been difficult without the help of Suzy Arbuckle and Raul Cunha, and we would like to express our special gratitude to them for their assistance.

Contents

1

Self-organized and self-assembled structures

Almost all systems we encounter in nature possess some sort of form or structure. It is then natural to ask how such structure arises, and how it changes with time. Structures that arise as a result of the interaction of a system with a template that determines the pattern are easy to understand. Lithographic techniques rely on the existence of a template that is used to produce a material with a given spatial pattern. Such pattern-forming methods are used widely, and soft lithographic techniques are being applied on nanoscales to produce new materials with distinctive properties (Xia and Whitesides, 1998). Less easily understood, and more ubiquitous, are self-organized structures that arise from an initially unstructured state without the action of an agent that predetermines the pattern. Such self-organized structures emerge from cooperative interactions among the molecular constituents of the system and often exhibit properties that are distinct from those of their constituent elements. These pattern formation processes are the subject of this book.

Self-organized structures appear in a variety of different contexts, many of which are familiar from daily experience. Consider a binary solution composed of two partially miscible components. For some values of the temperature, the equilibrium solution will exist as a single homogeneous phase. If the temperature is suddenly changed so that the system now lies in the two-phase region of the equilibrium phase diagram, the system will spontaneously form spatial domains composed of the two immiscible solutions with a characteristic morphology that depends on the conditions under which the temperature quench was carried out. The spatial domains will evolve in time until a final two-phase equilibrium state is reached. The evolution of such structures is governed by thermodynamic free energy functions, suitably generalized to account for the heterogeneity of the medium and the existence of interfaces separating the coexisting phases. The spontaneous formation of such structures is the system's response to an initial instability or metastability (Bray, 1994; Debenedetti, 1996; Dattagupta and Puri, 2004).
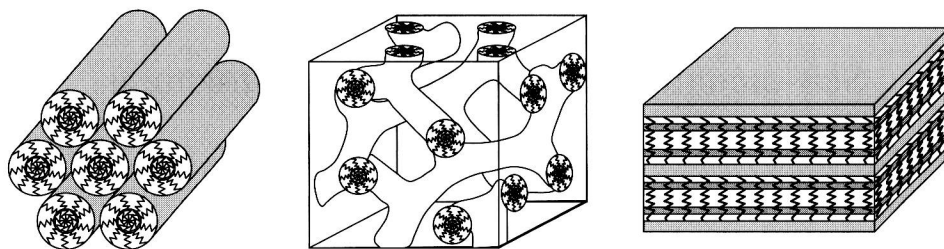
Fig. 1.1. Schematic depictions of hexagonal, gyroid and lamellar nanocomposites that result from the self-assembly of diacetylenic surfactants on silica. From Brinker (2004), p. 631, Figure 6a.

The formation of macroscopic coherent spatiotemporal structures arising from an initial instability or metastability is often a consequence of some inherent symmetry-breaking element. Fluctuations and conservation laws also play an important role in determining the character of the time evolution leading to self-organized structures. As the system evolves, interfaces which delineate the boundaries of local domains also move: thus an understanding of interface dynamics, and more generally of defect dynamics, is a central feature of the evolution of self-organized structures.

Ultimately, self-organized structures have their origin in the nature of the intermolecular forces that govern the dynamics of a system. In some instances, the connection between the macroscopic coherent structure and specific features of the intermolecular forces is rather direct. Self-assembly of molecular constituents in solution is such a process. Self-assembly leads to a variety of three-dimensional structures: strong hydrophobic attraction between hydrocarbon molecules can cause short chain amphiphilic molecules to organize into spherical micelles, cylindrical rod-like micelles, bilayer sheets, and other bicontinuous or tri-continuous structures (Fig. 1.1) (Gelbart *et al.*, 1994; Grosberg and Khokhlov, 1997; Brinker, 2004; Ozin and Arsenault, 2005; Pelesko, 2007). Self-assembly of long-chain block copolymers can also occur through microphase separation as a result of covalent bonds between otherwise immiscible parts of the polymer. This process can lead to three-dimensional structures with topologies similar to those of amphiphilic molecules (Fredrickson and Bates, 1996; Bates, 2005). Similarly, two-dimensional systems, such as Langmuir monolayers at a water–air interface or uniaxial ferromagnetic films, can self-assemble into unidirectional periodic stripes and hexagonally arranged circular drops as a result of the competition between long-range repulsive dipolar interactions and relatively shorter-range attractive van der Waals interactions. Monolayers on a metallic substrate can also self-organize into ordered structures (Fig. 1.2). The most direct way to model such self-assembly is by following the motions of the constituent elements by molecular dynamics. A number of different coarse-grain schemes have been devised in order to extend the size,
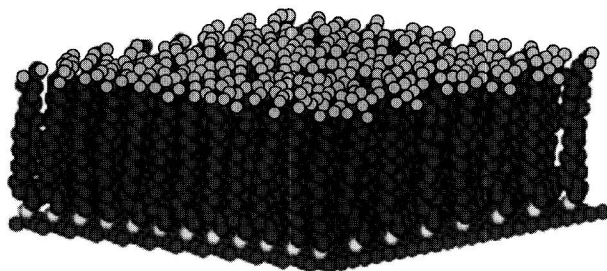
Fig. 1.2. Results of a molecular dynamics simulation of a densely packed assembly of 16-mercapto-hexadecanoic acid molecules tethered to a gold surface. From Lahann and Langer (2005), p. 185, Figure 2.
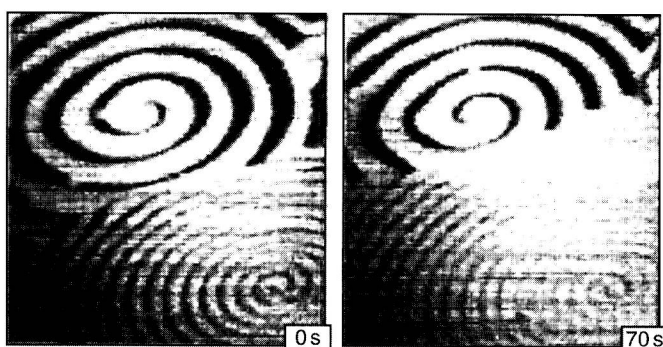

Fig. 1.3. Spiral wave CO oxidation patterns on the surface of a Pt(110) surface. Reprinted with permission from Nettesheim *et al.* (1993). Copyright 1993, American Institute of Physics.

length, and timescales of such simulations (Karttunen *et al.*, 2004; Nielsen *et al.*, 2004; Venturoli *et al.*, 2006). On mesoscopic scales self-assembly can be analyzed and understood through models based on free energy functionals and relaxational dynamics.

Self-organized structures also arise in systems that are forced by external flows of matter or energy to remain far from equilibrium (Nicolis and Prigogine, 1977; Kapral and Showalter, 1995; Walgraef, 1997; Manrubia *et al.*, 2004; Hoyle, 2006; Pismen, 2006). If chemical reagents are continuously supplied to and removed from a container where an oxidation reaction takes place on a catalytic surface, in many circumstances the chemical reaction does not occur homogeneously over the entire surface but instead proceeds by the propagation of chemical waves of oxidation that travel across the catalytic surface. The combination of nonlinear chemical kinetics and conditions that force the reaction to occur in far-from-equilibrium conditions is responsible for the existence of the evolving patterns of chemical waves seen on the surface of the catalyst (Fig. 1.3).

Biological systems almost always operate under far-from-equilibrium conditions since input of chemical and other energy sources is needed to maintain the living state. Consequently, the conditions for the appearance of self-organized structures are present in these systems. Indeed, the nonlinear chemistry associated with biochemical networks, in combination with diffusion of chemical species, can lead to the formation of chemical waves which are often implicated in the mechanisms responsible for biological function (Winfree, 1987, 2001; Murray, 1989; Goldbeter, 1996). Chemical waves are known to play a role in cell signaling processes leading to cell division, aggregation processes in colonies of the amoeba *Dictyostelium discoideum*, and the pumping action of the heart, to name a few examples. Perhaps even more interesting is the fact that chemical patterns have been observed in individual living cells (Petty *et al.*, 2000).

Although applications to fluid dynamics are not considered in this book, fluid flow also provides many examples of self-organized structures (Cross and Hohenberg, 1993; Frisch, 1995; Nicolis, 1995; Walgraef, 1997). The hexagonal patterns arising from Rayleigh–Bénard convection when a fluid is heated from below are familiar, as are the complex spatiotemporal patterns seen in turbulent fluids. In such cases, descriptions of the origins and dynamics of the patterns are usually based on an analysis of the Navier–Stokes equation; the instabilities are seen to emerge as a result of the convective nonlinear terms in this equation.

In contrast to equilibrium systems, in far-from-equilibrium systems free energy functions do not always exist, and the description of the dynamics of self-organized structures must be based on different premises. In the case of chemical and biochemical systems the starting point is usually a reaction–diffusion equation, while, as noted above, for fluid dynamics problems the Navier–Stokes equation is a natural starting point for the analysis.

In spite of the fundamental differences in the origins of diverse self-organized structures, there are often superficial similarities in their forms, and there exist common basic elements which are needed to understand their formation and evolution. At the macroscopic level, one needs a description in terms of suitable field variables or order parameters that account for the existence of spatial structure in the system. Other common elements include the presence of interfaces that separate phases or spatial domains that constitute the self-organized structure, and the existence of defects in the medium. Both of these features often control the dynamical evolution of the structure on certain time scales.

During the second half of the twentieth century, the concept of universality played a major role in our understanding of structural correlations and dynamics in condensed matter systems. Starting with Landau's unifying concept of the order parameter (Landau, 1937) and culminating in the renormalization group theory of critical phenomena (Wilson and Kogut, 1974), these developments demonstrated