

Elena Y. Vedmedenko

Competing Interactions and Patterns in Nanoworld



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and Patterns
in Nanoworld**

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Cover

Top left: Theoretically predicted phase domain wall in a quadrupolar system on a square lattice (see Chapter 2).

Bottom left: Schematic representation of the hexagonal ordering in a two-dimensional electron Wigner crystal at He surface (see Chapter 2).

Top right: Theoretically predicted vortex excitations in a magnetostatically coupled array of ferromagnetic nanoparticles on a triangular lattice (see Chapter 3).

Bottom right: Collage of experimental spin-polarized scanning tunnelling microscopy image of a phase domain wall in the antiferromagnetic Fe monolayer on W(001) and theoretically calculated magnetic structure of the domain wall (see Chapter 4).

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Preface

During my academic lifetime I have been in contact with several different scientific communities, including informatics, medical physics, and the physics of soft matter or magnetism. Each of these branches of science has long had a fascination with patterns, whether data ordering, memory patterns, coat patterns of animals, arrangements of molecules or spin configurations. The reason for the inexhaustible interest in the patterning on all length scales is three-fold: (i) it is recognizable and just beautiful; (ii) it is often unpredictable – that is, it contains a mystery; and (iii) any ordered structure is an encrypted message concerning the reasons for its formation. Thus, all the ingredients of a “good detective story” are at hand!

There are many exciting interpretations of this story in the literature. Most often, a tale begins with a description of a system in which a pattern has been observed, after which the mystery is lifted – at least partially – by a description of the microscopic properties of the system. Sometimes, this leads to a situation when one and the same pattern is known under diverse conditions, whilst all captivating names in different communities. Consequently, papers using different names are not cited, and phenomena are reinvented. Examples are the “micro-vortex structure”, “spin ice”, and “ $\pi/4 \pm n\pi/2$ configuration” – three notions all of which describe a ground state of a dipolar system on a square lattice in different systems. In a rarer and more general interpretation, the analysis is started with the depiction of a pattern, which is then characterized on the basis of an order parameter. The order parameter is an abstract construction and often is not directly related to the properties of a system. This may lead to a misinterpretation of the hidden message – that is, the physical or chemical grounds for pattern formation. For example, the organization of stripes is traditionally related to the competition between attractive- and repulsive interactions. However, a stripe pattern with the same order parameter can appear in a system with two repulsive couplings, or even for a single dipolar interaction in the presence of anisotropy. Thus, in order to decrypt the puzzles posed to us by Nature, an additional generalization by the type of interactions involved would be very helpful.

This idea appeared very clearly to me following the plenary lecture given by Professor J. Kirschner at the Annual Meeting of the German Physical Society in Dresden, March 2003. Professor Kirschner has demonstrated an experimental

model made from small magnets which were free to rotate on different lattices. The geometry of magnets and the model as whole has been adapted to represent pure dipolar systems. Both, the lecture and the model have attracted the vivid interest of researchers from a number of different fields. As the person responsible for construction of the model, I was confronted with diverse questions from the meeting participants with regard to interactions, lattice geometry, or the correspondence of the model to real physical systems.

This book is a systematic reply to a variety of questions addressed to me in Dresden. It is intended to serve as an introduction, for students and researchers alike, into the patterns arising in nanosystems caused by competing interactions. These interactions are classified into four main groups: (i) self-competing interactions; (ii) competition between a short- and a long-range interaction; (iii) competition between interactions on a similar length scale; and (iv) competition between interactions and anisotropy. Each class is further divided into subclasses corresponding to the localized and delocalized particles. For each subclass, concrete sets of interactions, corresponding patterns and microscopic details of systems where they appear are presented. Chapter 1 provides an introduction to modulated phases and models for their description, whilst in Chapter 6 several new advances in visualization of dynamical patterning are introduced.

The book can be read from cover to cover in order to explore the principles of self-organization and diversity of systems. However, it can be used as well in “cookbook” style – with a certain amount of cross-referencing – to obtain the recipe for structuring a particular set of interactions, lattice structure, and localization. For example, if the reader wishes to know which type of pattern appears in a spin system localized on a hexagonal lattice with antiferromagnetic first/second/third nearest-neighbor and ferromagnetic first/second/third nearest-neighbor interactions, he or she has simply to consult Chapter 4, which details the competition on a similar length scale for magnetic systems. Moreover, if the reader is interested in patterns arising in systems of moving charges or dipoles (e.g., electron gas or colloidal suspensions), he or she is referred to Chapters 2 or 3, depending on whether the short-range coupling between the particles exists.

This book is written at a fairly introductory level, for graduate or even undergraduate students, for researchers entering the field, and for professionals who are not practicing specialists in subjects such as statistical mechanics. Specialized terms are explained in the Insets, and patterns are visualized in many figures. My main aim was to write a readable text which can be understood without consulting numerous references, though for specialists in the field a vast body of literature is provided at the end of each chapter. I have also included a number of problems (with solutions provided!) at the end of each chapter for the reader to work through if he or she wishes. These problems can also be used by lecturers of applied mathematics, physics, or biology courses. Some of the problems are purely analytic, whereas others ask the reader to create a short program.

I would like to thank the editors, Michael Bär and Heike Höpcke at Wiley-VCH Verlag, not only for proposing the production of the book, but also for

their help. I am grateful to many colleagues and friends for fruitful discussions and suggestions, including Roland Wiesendanger, Jürgen Kirschner, Hans Peter Oepen, Kirsten von Bergmann, Andre Kubetzka, Matthias Bode, Oswald Pietzsch, Jean-Claude Lévy, Abdel Ghazali, Kai Bongs, Mykhaylo Kurik, and Stefan Heinze. I thank Nikolai Mikuszeit for the help with programming on “Mathematica” and discussions. I also sincerely thank my family for their great patience and support during the production of this book.

Hamburg, October 2006

Elena Y. Vedmedenko

1

Introduction

What distinguishes order from disorder? Some would argue that we experience structure as ordered only when the visual (aural) stimuli reveal patterns. If so:

- What are the physical reasons for the pattern formation?
- To what extent do the patterns observed in the world at large resemble those in the atomic world?
- What happens on the nanometer scale, in two- or even one-dimensional systems?
- Can the nanoscale patterns always be recognizable?
- What if the complexity of the patterns exceeds our powers of cognition?

In exploring these issues, I will first introduce experimental data on nano- and mesoscopic patterns, and then present the earliest theoretical models of pattern formation. We will then move on to investigate in detail the relationships between the patterns and the interactions within a material that operate on different length scales or in opposing/cooperating manners.

1.1

How the Story Began

Self-organization describes the evolution process of complex structures where ordered systems emerge spontaneously, driven internally by variations of the system itself. One can say that self-organized systems have order for free, as they do not require help from the outside to order themselves. Although the self-organization phenomena – for example, the formation of snowflakes or the stripes of zebras or tigers – were known empirically as early as Antiquity, it was only during the twentieth century that studies on that subject become more or less systematic. The very first publications on self-organization on the micrometer scale appeared in the surface chemistry due largely to the studies of I. Langmuir and, after the turning point in surface physics, when the first low-energy electron diffraction (LEED) experiments were conducted by C. J. Davisson and L. Germer in 1927. Nevertheless, rather few experimental investigations were carried out until the 1970s, this presumably being due both to the technological complexity of the measurements and the lack of an adequate theory. During the past 20 years, however, new – appar-

ently fundamental – patterns and superstructures on the nanometer scale have been discovered at an alarming rate. This advance was sparked in particular by the development of electron-, scanning tunneling, atomic force, friction force and magnetic force microscopies. However, despite several very good reviews [1, 2], editorial collections of articles [3, 4] and books [5–9], self-organization is still not considered to be a science in its own right. The reason for this is that there is a very wide spectrum of scientific directions, each with their own Lexis and goals, where the ordered superstructures appear. Thus, systematization of the patterns and reasons for their formation are necessary. As a first step in this direction, Section 1.1 provides a brief review of the earliest known micrometer/nanometer scale patterns, namely modulated structures and magnetic domains. Subsequently, in Section 1.2, the answer is provided to the first question listed above, namely “What are the physical reasons for pattern formation?”

1.1.1

Structure Periodicity and Modulated Phases

One is aware that many materials have an ordered structure and, indeed, the symmetry of the crystalline lattice, for example, is generally well known from X-ray experiments. These structures are very often periodic, with an ideal crystal being constructed by the infinite repetition of identical structural units in space. The philosophy of the life, however, is that all situations – the best and the worse – have their limits. All materials have surfaces, the physical properties of which differ from those of the bulk material due to the different atomic surroundings. It is said that a surface atom has a reduced (compared to the bulk material) coordination number that is nothing other than the number of nearest-neighbor atoms. But the question here is: “What type of structure should the surface atoms admit?”

During the 1920s this simple question gave rise to the new scientific directions of surface physics and chemistry. The answer was soon found, namely that as the surface atoms lost their neighbors in layers above, the surfaces are under tensile stress; that is, the surface atoms would prefer to be closer to their neighbors in the surface layer. This phenomenon, which exists in both liquid and solid materials, is known as *surface tension*. It determines the equilibrium shape of a body that is a minimum state of its surface tension. In a drop of liquid, the surface tension is isotropic, and hence the drop’s equilibrium shape is a sphere. When this drop is placed on top of a substrate the shape will usually change. In the case of a solid crystal, the answer to this question is not trivial because the surface tension is highly anisotropic. With some limitations, the surface tension of a solid or a liquid body can be calculated theoretically [10].

The existence of surface tension leads to a number of interesting structural phenomena [13]. One of these is the formation of surface domains with different atomic structure, while another is the formation of surface dislocations. In contrast to the bulk dislocations, which are linear defects inside a crystal lattice governing the plastic behavior of a material, the surface dislocations are concentrated mainly in the region beneath the topmost atomic layer (see Fig. 1.1 a). Many close-

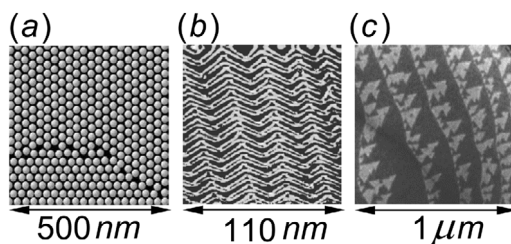


Fig. 1.1 (a) Schematic representation of a surface dislocation. (b) Scanning tunneling microscopy (STM) image of the Au(111) reconstruction; adapted from [11]. (c) Low-energy electron microscopy (LEEM) image of the reconstruction that occurs on Si(111) surface; adapted from [12].

packed metal systems show patterns of surface dislocations, which form in order to relieve the strain between an overlayer and a bulk crystal. Indeed, the well-known herringbone reconstruction of a clean gold (111) surface [11] [see Inset 1.1 and Fig. 1.1b] is a striking example of such a dislocation pattern, formed because the lower coordinated surface gold atoms have a closer equilibrium spacing than normally coordinated bulk gold atoms. The “herringbone” pattern of Figure 1.2b is comprised of “double stripes”, the orientation of which changes periodically. Each double stripe consists of a wide face-centered cubic (*fcc*) domain and a narrower hexagonal close-packed (*hcp*) domain, separated by domain walls where atoms sit near the bridge sites. Atoms at bridge sites are pushed out of the surface plane, and thus show up as light regions on scanning tunneling microscopy (STM) images. Hence, the stripe contains two partial misfit dislocations. To form the herringbone out of the double stripe, the stripes must bend at the “elbows”. There are additional point dislocations at pointed elbows.

Another prominent example of the surface reconstruction give the reorientation of the surface atoms that occur on Si(111) surface below a temperature of 860 °C [14]. Figure 1.1c illustrates a low-energy electron microscopy (LEEM) image of that type of reconstruction. The contrast between light and dark regions illustrates the sharp division between ordered (light) and disordered (dark) phases. Both patterns are periodic and can be usefully described in terms of larger than atomic basic structural units or modules. There exist many other complex systems which

Inset 1.1 Crystallographic directions

Cutting and polishing a single crystal defines a certain surface. The orientation of the surface (the arrow in Fig. 1.2) with respect to the crystallographic structure is usually given by a number in brackets (Miller indices) [15]. For the gold crystal of Figure 1.1a it was the “(111)”—surface. In this drawing, the *desired* direction of the cut is symbolized by the blue line. The *actual* cut always has a slight error (green dashed line). This results in a surface with monoatomic steps. The surfaces with a miscut are also called *vicinal surfaces*.

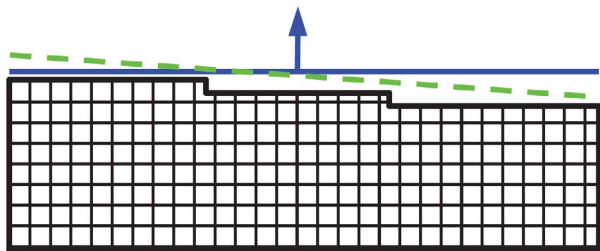


Fig. 1.2 Single crystal with a miscut resulting in monoatomic steps. The blue arrow denotes the orientation of the ideal surface with respect to the crystallographic structure (see Inset 1.1).

may be also systematized in terms of periodic series of stacking variants of the simple subunits; these structures are often denoted as “arrays”.

An important example of periodic surface structures gives thin epitaxial films and nanoscale self-assembly on solid surfaces. Epitaxial films are usually obtained by depositing of a material on top of a single crystal (substrate) on which it can be investigated. Material deposited on top of the substrate may cover it, thus forming a smooth film or so-called “islands”. Whether a smooth film or islands are formed depends critically on the properties of the substrate, the deposited material, and the temperature. Remember “water on glass”: if the glass is slightly dirty, the water forms a film on it; however, on fresh cleaned glass the formation of drops is favored. The islands themselves also often represent single crystals, and have an ordered superstructure. Figure 1.3 provides an example of ordered metallic epitaxially grown nanoarrays in three different systems. However, in the area of the organic and the molecular epitaxy, very successful self-assembly techniques have been also elaborated [16, 17]. Of course, there are many other nano-, meso- and macroscopic systems where the self-organized arrays can be identified. However, the aim of this section is not to provide a complete review of the modulated structures, but rather to determine how they should be described.

As could be seen, the self-organized surface structures possess certain periodicity. The periodicity has at least two length scales – that of the atomic lattice inside of the islands or domains, and that of an array. Such structures, which consist of a perfectly periodic crystal, but with an additional periodic modulation of some order parameter, are denoted as *modulated structures*. An important question is, “How the periodicity of the order parameter is related to the periodicity of the underlying bulk crystal?” If atoms or molecules are weakly bonded to a surface, the structure they adopt – even periodic – may be almost completely independent of the lattice structure of the substrate. The periodicity is then dictated almost solely by the interparticle interactions. If the adsorbed particles have a strong bonding to the surface, they may be arranged with the same lattice structure as the substrate. Often however, because of lattice mismatch or tensile strain, the overlayer has a lattice structure, which differs from

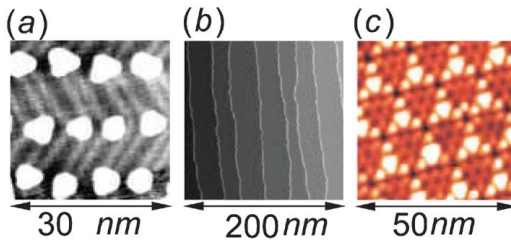


Fig. 1.3 (a) Flat Co dots on the herringbone reconstructed Au(111) surface, that are obtained in the subatomic-monolayer regime; reprinted with permission from [18]. (b) STM image of the Fe nanowires on the W(110) surface; reprinted with permission from [19]. (c) STM image of the In/Ag alloy cluster array fabricated on Si(111)-(7×7) surface; reprinted with permission from [20].

that of substrate. If the lattice vectors of the top layer are *rationaly related* to the substrate lattice vectors, such a structure is denoted as a “commensurate”. In the case of an *irrational relation* between the overlayer and the substrate lattice vectors, one says that an “incommensurate” structure is formed. Many surface layers – for example herringbone reconstruction and epitaxially grown systems – adopt incommensurate structures, and consequently the questions arise:

- Are the modulated structures – and particularly incommensurate configurations – thermodynamically stable, or are these some disturbed, metastable states?
- What is the physical mechanism underlying the formation of modulated phases?

These questions will be answered in Section 1.2.1.

1.1.2

Ferromagnetic and Ferroelectric Domains

Materials whose atoms carry strong magnetic/electric moments are called *ferromagnets* and *ferroelectrics*, respectively. Many different substances demonstrate ferromagnetic and/or ferroelectric properties. For example, iron, nickel, cobalt and some of the rare earth metals (e.g., gadolinium, dysprosium) exhibit ferromagnetism, with iron (ferric) being the most common and most dramatic example. Samarium and neodymium in alloys with cobalt are used to fabricate very strong rare-earth magnets. Among the different ferroelectrics, oxides showing a perovskite or a related structure are of particular importance.

Ferromagnetic/ferroelectric materials possess their properties not only because their atoms carry a magnetic/electric moment, but also because the material is composed of small regions known as magnetic/ferroelectric domains. The concept of domains was first introduced by Weiss, in his famous study [21].

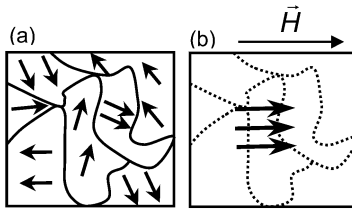


Fig. 1.4 (a) Weiss domains, the total magnetization of the sample is zero. (b) The domains are aligned under the action of the external magnetic field H ; the total magnetization has a finite value.

In each domain, all of the atomic dipoles are coupled together in a preferential direction (see Fig. 1.4). This alignment develops during solidification of a crystal from the molten state, during an epitaxial growth, or during the ordering of a liquid mixture. Ferromagnetic materials are said to be characterized by “spontaneous” magnetization as they obtain saturation magnetization in each of the domains without an external magnetic field being applied. Even though the domains are magnetically saturated, the bulk material may not show any signs of magnetism because the domains are randomly oriented relative to each other (Fig. 1.4a). Ferromagnetic materials become magnetized when the magnetic domains are aligned (Fig. 1.4b); this can be done by placing the material in a strong external magnetic field, or by passing electrical current through the material. The more domains that are aligned, the stronger the magnetic field in the material. When all of the domains are aligned, the material is said to be saturated, and no additional amount of external magnetization force will cause an increase in its internal level of magnetization. At the start of the 20th century the domains were introduced only as an abstract construction to explain:

- that below the critical temperature, the total magnetization of a magnet is not the same as its saturation magnetization;
- that a permanent magnet can be made from a ferromagnetic material by applying a magnetic field;
- the hysteresis and necessity for a coercive field to remove any net magnetization;
- the zero average magnetization and non-zero local magnetization of a ferromagnet [22].

Despite this very useful phenomenological theory of magnetic domains, the mechanism of the domain formation remained obscure until the 1930s.

In the seminal report by Landau and Lifshitz in 1935 [24], the domains were proposed to originate from the minimization of the magnetostatic energy stemming from the dipolar interaction. Since then, a wide variety of two-, three- and even one-dimensional physical-chemical systems, which display domain patterns in equilibrium [2], has been found. Among these are ferroelectrics [25], liquid crystals [26], block-copolymers [26], ferrofluids [27], Langmuir layers [28], superconductors [29], and other related systems. The domains can have peri-

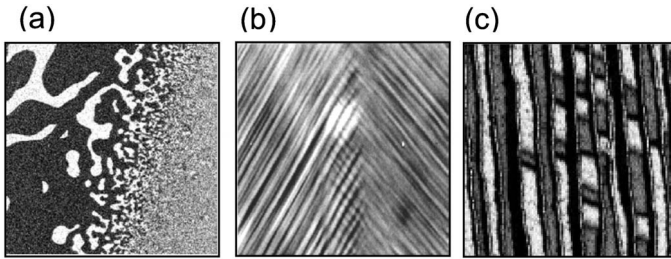


Fig. 1.5 (a) Scanning electron microscope with polarization analysis (SEMPA) images of magnetic domain structures in a wedge-shaped Co/Au(111) film; reprinted with permission from [31]. Dark and light regions represent areas of antiparallel magnetization. The smallest domain size is 300 nm. (b) Typical fragment of a domain pattern in electrically poled along the [001] direction ferro-

electric $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_{3-x}\text{PbTiO}_2$ crystal observed in a polarizing microscope; adapted from [23]. The typical domain size is 20 μm . (c) STM image of the magnetic domains (dark and light gray areas) and domain walls (black lines) in Fe/W(110) nanowires; reprinted with permission from [19]. The typical domain size is 20 nm.

odic, random or incommensurate superstructure. Nowadays, nanometer-sized magnetic [19, 30, 31] and ferroelectric [23] domains, which cannot be expected from the original theoretical concepts, have been discovered (Fig. 1.5). The explanation of the origin of those domain nanopatterns requires new theoretical concepts, which will be addressed in Section 1.2.2.

1.2 First Theoretical Approaches for Competing Interactions

1.2.1

Frenkel–Kontorova Model

One of the earliest theories of a system with competing length scales is known as the Frenkel–Kontorova (FK) model. This was introduced more than half a century ago [32, 33] in the theory of dislocations in solids to describe the sim-

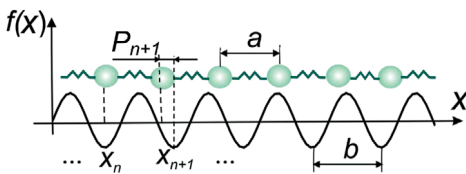


Fig. 1.6 Schematic representation of the Frenkel–Kontorova model. The balls represent surface atoms bonded with neighboring atoms by the interatomic interactions (Hook’s springs of natural length a) and with the substrate through the potential V (solid black line) of periodicity b .