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-

Competing Interactions and Patterns in Nanoworld. Elena Y. Vedmedenko

ISBN: 978-3-527-40484-1

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 tight. 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-

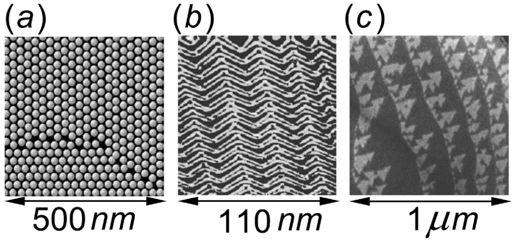


Fig. 1.1 (a) Schematic representation of a surface dislocation. (b) Scanning tunneling microscopy (STM) image of the Au(111) reconstruction; adapted from [11]. (c) Low-energy electron microscopy (LEEM) image of the reconstruction that occurs on Si(111) surface; adapted from [12].

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. 1.1 b] 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 1.2 b 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 1.1 c 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 1.1 a 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.*

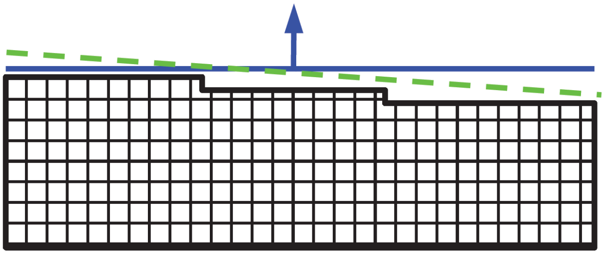


Fig. 1.2 Single crystal with a miscut resulting in monoatomic steps. The blue arrow denotes the orientation of the ideal surface with respect to the crystallographic structure (see Inset 1.1).

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

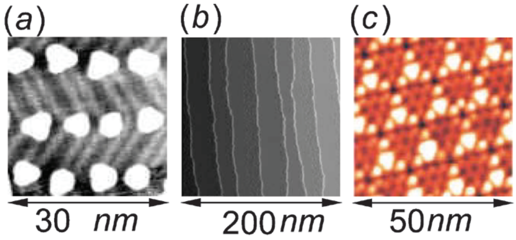


Fig. 1.3 (a) Flat *Co* dots on the herringbone reconstructed Au(111) surface, that are obtained in the subatomic-monolayer regime; reprinted with permission from [18]. (b) STM image of the *Fe* nanowires on the W(110) surface; reprinted with permission from [19]. (c) STM image of the In/Ag alloy cluster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

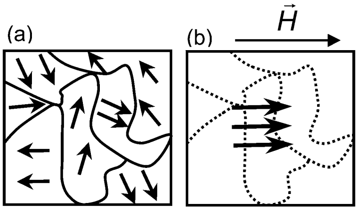


Fig. 1.4 (a) Weiss domains, the total magnetization of the sample is zero. (b) The domains are aligned under the action of the external magnetic field *H*; the total magnetization has a finite value.

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. 1.4 a). Ferromagnetic materials become magnetized when the magnetic domains are aligned (Fig. 1.4 b); 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-

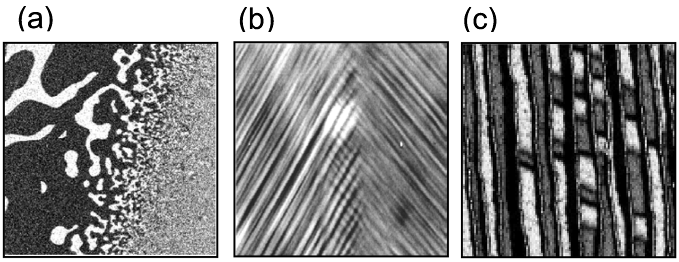


Fig. 1.5 (a) Scanning electron microscope with polarization analysis (SEMPA) images of magnetic domain structures in a wedge-shaped Co/Au(111) film; reprinted with permission from [31]. Dark and light regions represent areas of antiparallel magnetization. The smallest domain size is 300 nm. (b) Typical fragment of a domain pattern in electrically poled along the [001] direction ferroelectic $Pb(Mg_{1/3}Nb_{2/3})O_{3-x}PbTiO_2$ 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-

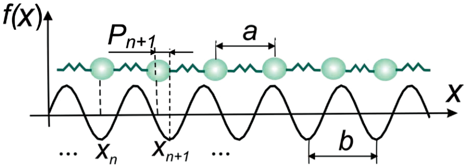


Fig. 1.6 Schematic representation of the Frenkel–Kontorova model. The balls represent surface atoms bonded with neighboring atoms by the interatomic interactions (Hook's springs of natural length *a*) and with the substrate through the potential *V* (solid black line) of periodicity *b*.

plest situation when the surface atomic layer is assumed to contain a dislocation (see Fig. 1.1). Subsequently, this model has been used extensively for the modeling of nonlinear dynamical processes in a variety of condensed matter [34, 35] and biophysical [36] systems. As the FK model captures the essential physics of many different problems, it is broadly used in present-day research investigations into metal surfaces [37, 38], atomic friction [39, 40], biological [41, 42] and quantum [43] systems.

The surface layer in the FK approach is modeled by a chain of balls (atoms) connected by harmonic Hook's springs of natural length a and stiffness k. The bottom solid is assumed to be rigid, so that it can be treated as a fixed periodic substrate potential V (Fig. 1.6) – that is, the surface/interface part of a crystal can be sheared with respect to the bulk material.

Inset 1.2 Solitons

The word "soliton" was first used to describe nonlinear waves interacting as particles [44]. In fact, the term soliton almost became "solitRon", as an abbreviation for the "solitary wave", but at the time a company was trading with the identical name, and hence the 'r' had to be removed. The history of studying solitons began in August 1834, when the Scottish engineer John Scott Russell observed a large solitary wave in the Union Canal near Edinburgh. In the days of Russell there were many debates concerning the very existence of that type of solitary wave, but today many complex dynamic systems throughout science are known to possess soliton solutions: from hydrodynamics to nonlinear optics; from plasmas to shock waves; from tornados to the Great Red Spot of Jupiter; from the elementary particles of matter to the elementary excitations.

The physics of the model is determined by competition between the elastic energy, which favors incommensurate (see Section 1.1.1) separation between atoms, and the tendency for the atoms to sit at the bottom of potential wells, leading to a commensurate structure. The competition can lead to an interesting situation when the surface atoms are neither ordered (as at the top of Fig. 1.1 a) nor disordered (as beans spilled upon a table), but rather form a nontrivial pattern of assembled atoms. The exciting question here is what this pattern should look like, and how it depends on the parameters of the FK model.

The periodic force of the substrate has the form (Fig. 1.6) $f(x) = V_0 \sin\left(\frac{2\pi x}{b}\right)$, V_0=const. The elongation of the string from its natural length a is $x_n - x_{n-1} - a$ and, consequently, the Hook's force between two neighboring atoms (Fig. 1.6) is $f_H(x) = -k(x_n - x_{n-1} - a) = -k(x_{n+1} - x_n - a)$.

The potential energy corresponding to a conservative force $F(x)$ is known to be $U(x) = -\int_{x_0}^{x} F(x)dx + U(x_0)$. As $f(x)$ and $f_H(x)$ are not path-dependent they are conservative. Hence, if $U(x_0) = 1$, the energy of a configuration $U(x)$ or, in other words, the Hamiltonian of the whole systems can be written as

$$H = \sum_n \left[\frac{1}{2} k (x_{n+1} - x_n - a)^2 + V(1 - \cos(2\pi x_n / b)) \right] \tag{1.1}$$

with $V = V_0 \cdot 2\pi/b$ the amplitude of the potential. It is helpful to introduce a phase P_n, which measures the position of the atoms relative to the minima of the potential (Fig. 1.6). P_n can be either positive or negative. Then, the atomic coordinate is defined by:

$$x_n = nb + bP_n/2\pi \, , \tag{1.2}$$

$$\cos(2\pi x_n/b) = \cos(2\pi n + P_n) = \cos P_n \tag{1.3}$$

and the elongation of a string between n and n–1 balls becomes

$$x_n - x_{n-1} - a = P_n - P_{n-1} - 2\pi \cdot (a - b)/b \, . \tag{1.4}$$

The expression $d = 2\pi \cdot (a - b)/b$ measures the misfit between two competing length scales a and b; $P_n - P_{n-1}$ gives the mismatch between the equilibrium positions of the atoms and the periodicity of the cosine potential (i.e., it represents the heart of the problem).

For a strong interatomic potential $k \gg 1$ in Eq. (1.1) the displacement of atoms from the corresponding potential minima is a smooth function of the coordinate and can be treated in continuum limit

$$P_n - P_{n-1} = dP/dn \, . \tag{1.5}$$

With (1.5) the equation (1.1) transforms to

$$H = \int \left\{ \left(\frac{dP}{dn} - d \right)^2 /2 + V(1 - \cos P) \right\} dn \, . \tag{1.6}$$

Minimization of the energy H is equivalent to finding a solution of

$$\partial^2 P / \partial n^2 = V \sin P \, , \tag{1.7}$$

which is the one-dimensional sine-Gordon equation, a special case of the time-dependent sine-Gordon equation $\frac{\partial^2 P}{\partial t^2} + \frac{\partial^2 P}{\partial n^2} = V \sin P$ with t – the time.

Inset 1.3 Numerical approximation of the sine-Gordon equation

$$\frac{\partial^2 u}{\partial t^2} - \frac{\partial^2 u}{\partial x^2} + \sin(u(x,t)) = 0 \quad \text{using difference equations}$$

1) Defining of the coordinate-time rectangle (see sketch below);

2) $u_{ij} = u(x_i, t_j)$;

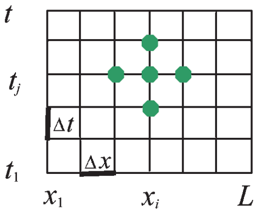
3) $$\frac{\partial^2 u(x,t)}{\partial t^2} = \frac{u_{i,j+1} - 2u_{i,j} + u_{i,j-1}}{\Delta t^2}$$

4) $$\frac{\partial^2 u(x,t)}{\partial x^2} = \frac{u_{i+1,j} - 2u_{i,j} + u_{i-1,j}}{\Delta x^2}$$

5) $r = \dfrac{\Delta t}{\Delta x}$

initial position function $u_{i,1} = f(x_i)$

1st derive velocity function $u^t_{i,1} = g(x_i)$



6) $$u_{i,2} = f(x_i)(1 - r^2) + g(x_i)\Delta t + \frac{r^2}{2}(f(x_{i+1}) + f(x_{i-1})) - \sin(f(x_i))$$

$$u_{i,j+1} = f(x_i)(2 - 2r^2) + g(x_i)\Delta t + r^2(u_{i+1,j} + u_{i-1,j}) - \sin(u_{i,j})\Delta t^2$$

For further details see [45].

Solutions of that equation are known from mathematics and physics of nonlinear phenomena [46]. The simplest are the “kink” (the black curve at the top of Fig. 1.7) and the “anti-kink” (the black curve at the bottom of Fig. 1.7) solitons (see Inset 1.2). A kink is a solution whose boundary value at the left infinity is 0 (–π), and at the right infinity is 2π (+π); the boundary values of an anti-kink are 0 (+π) and –2π (–π), respectively (black curves in Fig. 1.7). Physically, this means that the atomic displacement from the position of a potential well P_n is 0 or 2π at the boundary – that is, the atoms are placed in the wells. These are all light-blue atoms in Figure 1.7. Inside of the kink (anti-kink), the displacements P_n are different as from both 0 and 2π; these are the dark-blue atoms in Figure 1.7. In our case, the kink describes a vacancy in the chain (as in Fig. 1.7, top), while the anti-kink corresponds to excess particles (as in Fig. 1.7, bottom). Thus, the kink-solutions model two simplest types of dislocations.

For a weak interatomic potential $k<1$ (see Eq. (1.1)) the kink becomes very narrow and, therefore, essentially discrete. As a matter of fact, only very few atoms lying near the center of the kink (anti-kink) have different from 0 or 2π displacements P_n. In that case, Eq. (1.1) must be solved discretely. To do so, one rewrites the elongation of a string (see Eq. (1.4)) as

$$x_{n+1} - x_n - a = x_{n+1} - x_n - (x_n - x_{n-1}) = x_{n+1} - 2 \cdot x_n + x_{n-1} \tag{1.8}$$

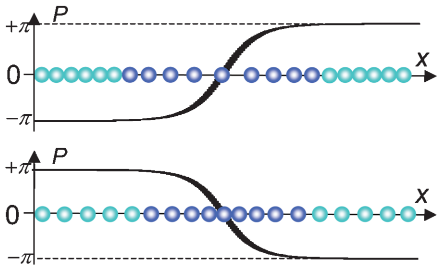


Fig. 1.7 Schematic representation of the "kink" (top of the figure) and "antikink" (bottom of the figure). While the balls show real space displacements of the atoms, the black curves correspond to the function $P_i=f(x)$, where P_i is displacement of the i-th atom.

and Eq. (1.1) as

$$H = \sum_n \left[\frac{1}{2}k(x_{n+1} - 2\cdot x_n + x_{n-1})^2 + V(1-\cos(2\pi x_n/b))\right]. \qquad (1.9)$$

The right-hand part of Eq. (1.8) is nothing else than the central difference approximation to the second-order derivative, and can be solved numerically (see Inset 1.3 and Exercise 1). The FK problem in the discrete case is more complicated than the previous one, as it may have unstable solutions [45]. For different boundary conditions and different parameters of the model, more complicated solutions than a simple kink exist. These are sequences of kinks or anti-kinks – that is, the lattice of domain and domain walls is formed (Exercise 1). As the kinks-series is similar to stairs, it had become a rather colorful name: the "devil's staircase" (see Exercise 1). Besides this unusual name, this result leads to a very important conclusion – that the perfect crystal ordering is not always the most stable! Over a certain range of temperatures, pressures, etc., crystals or crystal surfaces can spontaneously exhibit a periodic modulation which is not always a rational combination of the natural periods of the crystal. Examples of such a configuration are shown in Figures 1.1 b, 1.6 and 1.7.

1.2.2
Theoretical Models of the Magnetic/Ferroelectric Domains

The term "domains" can be used in different contexts. In Section 1.1.1, this notation was used to describe those regions of a crystal with different atomic structures. In the context of the present section, however, a crystalline structure is the same everywhere, while the orientation of spontaneous polarization in different domains is different. Although the complete mechanism of the formation of magnetic/ferroelectric domains is rather complex, the main principles can be understood on the basis of phenomenological conception of the exchange and the dipolar energy. Therefore, although in the next section I will provide a basic notion of these energies, they will be described in more detail in the following chapters.

1.2.2.1 Phenomenology of the Dipolar Interaction

In the first approximation, a magnet or a ferroelectric can be successfully treated as an ensemble of atomic magnetic or electric moments (dipoles). Each dipole can be modeled as a pair of magnetic/electric charges of equal magnitude but opposite polarity, or as an arrow representing the direction of a moment. The moments are known to align themselves in an external magnetic or electric field (just as a compass needle in the magnetic field of the Earth). As every moment itself is a source of a field (Fig. 1.8), it can be aligned in the field of any other dipole and vice versa – that is, the moments interact. The space distribution of the field produced by a dipole is nonlinear. The strength of magnetic or electric field is a vector quantity; it has both magnitude and direction, and is also rather weak. The strength of a dipolar interaction between two dipoles is of order of few degrees Kelvin. The magnitude of the dipole field decreases with distance as $1/r^3$, while its direction depends on the relative positions and orientations of atomic moments (Fig. 1.8). As a crystal consists of milliards of atoms, each atomic dipole experiences the action of milliards of fields with different direction and amplitude coming from all other dipoles (see Fig. 1.8). The total field acting on a moment can be determined as a vector superposition of all atomic fields. Because of the long-range character and position-dependence of the field distribution, a low-energy configuration of a pure dipolar ensemble is fairly difficult to predict. Some of the striking features of the dipolar coupling, however, can be derived even on the basis of school-level physics.

It is widely known that opposite charges attract whilst unlike charges repel each other, or that two bar magnets are attracted the North to the South pole. Why is this? Two separate magnets have two South and two North poles – together, four uncompensated poles. But two coupled bar magnets have only one South and one North pole – the other two poles are compensated. Hence, by means of attraction, the so-called surface charges – that is, the charges on an open surface – are minimized. The surface charge minimization leads to the de-

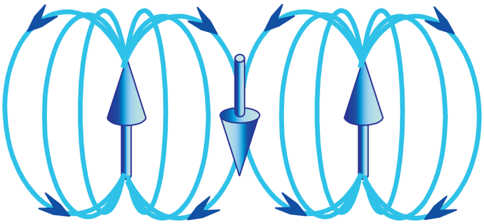


Fig. 1.8 An energetically favorable orientation of a dipole in the field of two other dipoles.

crease of the magnetic/electric field and, hence, to a decrease in the total energy. Thus, one of the main features of dipolar interaction is that this coupling attempts by all means to avoid free poles. This feature, which is referred to as the "pole avoidance principle" [47], is very important when explaining domain formation.

1.2.2.2 **Phenomenology of the Exchange and Exchange-Like Interactions**

As the dipolar interaction is rather weak it cannot serve as a reason for spontaneous magnetization or polarization at room temperature. Hence, aside from the dipolar coupling, there should exist another, much stronger coupling, and for a magnet this is the quantum mechanical exchange interaction. Without going into details, the exchange coupling between two neighboring magnetic ions will force the individual moments into either parallel (ferromagnetic) or antiparallel (antiferromagnetic) alignment with their neighbors. Such coupling is very strong (of the order of $10 \ldots 10^3$ K), but is of short range – that is, it decreases rapidly as the ions (atoms) are separated. The direct exchange interaction in its simplest form can be described by the Heisenberg Hamiltonian [48]:

$$H_{\text{ex}} = -2J \sum_{\langle i,j \rangle} \mathbf{S}_i \cdot \mathbf{S}_j$$

where J is the exchange coupling constant which is non-zero only for nearest neighbor spins S. For a ferromagnet, J is positive, that is H_{ex} has its minimum for parallel spins; however, for an antiferromagnet J is negative and H_{ex} has its minimum for antiparallel spins.

A ferroelectric crystal is a crystal which exhibits an electric dipole moment even in the absence of an external electric field. The spontaneous ferroelectric polarization arises due to distortion of the primitive crystal cell inducing the displacement of positive and negative ions with respect to each other. The charge displacement leads to the formation of strong molecular dipoles oriented along certain crystallographic directions. If it is possible to reorient the spontaneous polarization of a material between crystallographically equivalent states (so-called "variants") by an external electric field; then, in analogy to ferromagnets, one speaks about ferroelectrics. In ferroelectrics, nearest neighboring moments prefer to be collinear, as a non-collinear configuration requires changes in the geometry of neighboring crystalline cells that would produce a huge strain in the crystal. Thus, elastic strain energy in ferroelectrics acts similarly to ferromagnetic exchange [25, 49, 50]. As in the case of magnetism, the electric dipoles may also orient themselves in an antiparallel fashion, in which case the associated dipoles create an antiferromagnetic order. Two types of the ferroelectric order are shown schematically in Figure 1.9.

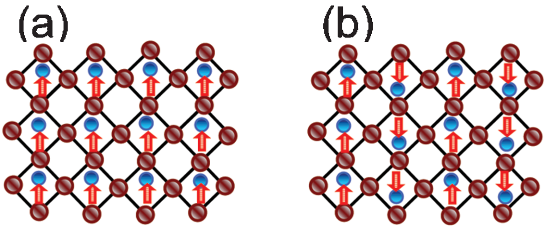


Fig. 1.9 Schematic diagram of (a) a ferroelectric and (b) an antiferroelectric with perovskite structure. The brown circles represent the sublattice with positive charges; the blue dots are negative ions. The red arrows show the direction of electric polarization of a cell. The polarization arises due to the displacement of negative charges from the center of an atomic cell.

1.2.2.3 **Mechanism of the Domain Formation**

It was highlighted in Section 1.2.2.1 that the dipolar interaction is very weak compared to the exchange coupling or strain. However, the exchange interaction is quite short-ranged, whereas the dipolar interaction is not. As a result, the total dipolar energy becomes significant when enormous numbers of dipoles are involved, and can compete with the stronger exchange coupling. In particular, a uniformly magnetized configuration such as that in Figure 1.4b or Figure 1.9a is highly uneconomical in terms of dipolar energy as it has fully uncompensated surfaces. The poles at the surface can be avoided and, thus, the dipolar energy substantially reduced by dividing the specimen into uniformly magnetized domains, the magnetization vectors of which point in opposite or widely different directions. Such a subdivision is paid for in exchange energy, since near the boundary of two domains the neighboring moments will have a rather large mutual angle. However, the region where non-collinearity occurs is very narrow because of the short range of the exchange interaction. In contrast, the gain in dipolar energy of every dipole drops when the domains are formed. Therefore, provided that the domains are not too small compared to the boundary between them (the so-called domain wall), domain formation will be favored. Thus, a lowering of the dipolar energy of the whole sample will compensate for the rise in exchange energy in the domain walls.

There are many different types of domains and domain walls. In the simplest case, the magnetization in domains have antiparallel orientation, and consequently the moments in the two domains always lie in equivalent crystallographic directions. Such domains are separated by the so-called 180° domain walls, which occur in virtually all materials and are distinct from all other non-180° walls in that they are not affected by stress [51]. The 180° walls can be also of different type, depending on the manner in which the magnetization rotates between two stable orientations. A comprehensive description of magnetic walls for beginners is provided by Jiles [52], while a more in-depth study is provided by Hubert and Schäfer [53]. In many cases, the so-called Bloch wall – where

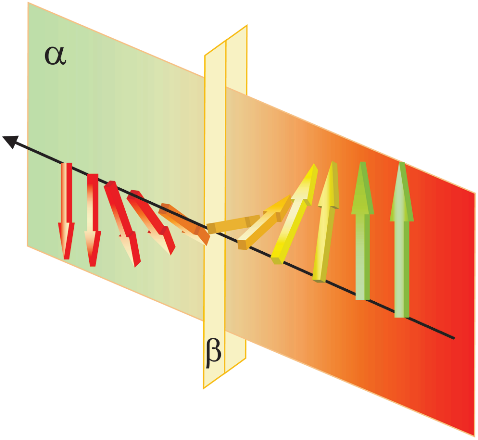


Fig. 1.10 Schematic representation of a Bloch domain wall.

magnetic moments rotate in the plane perpendicular to that of the stable magnetization in domains (Fig. 1.10) – has a lowest possible energy. The period of magnetization rotation in that simple case is 2π and is, usually, a multiple of a lattice constant (Fig. 1.10); that is, it has a commensurate structure. In some more complicated cases, however, so-called helical or "spin-wave"-like magnetic structures can occur [54]. In such structures the domains pass smoothly one into another, and the magnetization rotates in a helicoidal form along certain crystallographic directions. One can visualize a helical structure as an infinite sequence of Bloch walls. For such a structure, the period of rotation of the magnetization is not necessarily a rational multiple of the lattice constant as the beginning of a period can lie in-between two atomic sites.

Thus, in addition to atomic incommensurability, incommensurate magnetic structures can also appear.

1.3
Summary

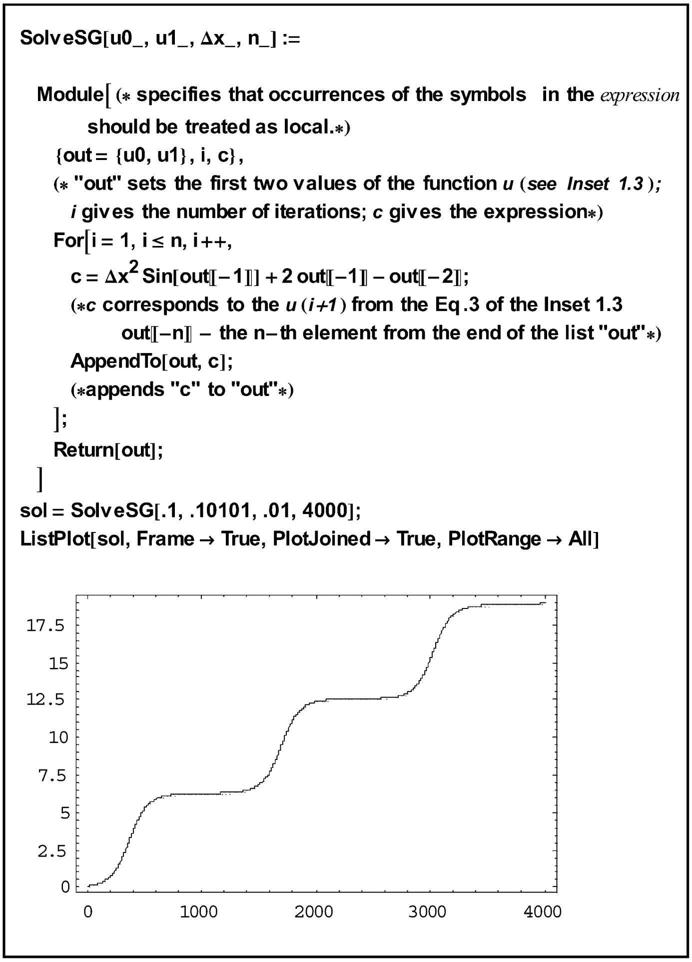
Now, we are able to answer the question that was posed in Section 1.1 concerning the *physical reasons for the pattern formation*. The self-organization of subunits of different nature – whether atomic or magnetic/electric – into ordered patterns is due to the competing interactions. The competition between different energies often leads to the spontaneous formation of modulated structures, the period of which is not always a rational combination of the natural periods of the crystal. For certain range competing energies, incommensurate phases appear.

1.4
Exercises

1. Check numerically that Eq. (1.10) really gives a “devil staircase” of kinks or anti-kinks in a one-dimensional system.

Solution

Listed below (see Fig. 1.11), Mathematica Notebook permits us to solve numerically a one-dimensional (no time-dependence) sine-Gordon equation (Eq. 1.7). In this simple example, Neumann-like boundary conditions are used. The first two values u_0, u_1 of the function u are fixed, while the next n values are calculated using difference equations method (see Inset 1.3).



```
SolveSG[u0_, u1_, Δx_, n_] :=

  Module[(* specifies that occurrences of the symbols  in the expression
        should be treated as local.*)
   {out = {u0, u1}, i, c},
   (* "out" sets the first two values of the function u (see Inset 1.3);
     i gives the number of iterations; c gives the expression*)
   For[i = 1, i ≤ n, i++,
     c = Δx^2 Sin[out[[-1]]] + 2 out[[-1]] - out[[-2]];
     (*c corresponds to the u(i+1) from the Eq.3 of the Inset 1.3
           out[[-n]] - the n-th element from the end of the list "out"*)
     AppendTo[out, c];
     (*appends "c" to "out"*)
   ];
   Return[out];
  ]
sol = SolveSG[.1, .10101, .01, 4000];
ListPlot[sol, Frame → True, PlotJoined → True, PlotRange → All]
```

Fig. 1.11 The Mathematica Notebook.

2. Decreases or increases the number of domains/domain walls with increasing strength of the dipolar interaction relative to the strength of the exchange coupling?

Solution
The number of domains increases as with decreasing exchange interaction the energy losses due to the formation of domain walls become smaller.

3. The paradigm of a periodic function is the trigonometric function sin(x), which is periodic with period 2π, i.e., $\sin(x + 2\pi) = \sin(x)$. Consider the sum of two sine functions

$$f(x) = \sin(x) + \sin(cx) = 2\sin\left(\frac{1+c}{2}x\right)\cos\left(\frac{1-c}{2}x\right)$$

where c is some fixed number. Is the function $f(x)$ always periodic? For which c the function $f(x)$ is aperiodic?

Solution
The periodicity depends on the values of c. If c is a rational number, $c = m/n$ with coprime integers m and n then the periods 2π (for sin(x)) and $2\pi c = 2/n$ (for sin(cx)) are commensurate, and the function is periodic with period as $2\pi n$ as $\sin[c(x + 2\pi n)] = \sin(cx + 2\pi m) = \sin(cx)$. However, if c is irrational, e.g., $c = \sqrt{2}$, the two frequencies are incommensurate, and $f(x)$ is aperiodic. Still, $f(x)$ retains much of its regularity – after all, it is simply the sum of two sine functions. It shows a so-called superstructure. Several examples of such superstructures have been provided in Sections 1.1.1 and 1.2.1. Another comprehensible example of the incommensurable structures is provided in [55].

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