

## Chapter 2

# Influence of Mathematics on Materials Science Upto Date

**Abstract** This chapter discusses the historical influence of mathematics on materials science and mathematical techniques and tools widely used in materials science today. There were many occasions in the past when mathematics and materials science met and interacted to inspire advances. From ancient times, humans are believed to have had an empirical knowledge of materials that was related to mathematics, such as awareness of crystal shape. Such knowledge probably played some basic role in the understanding of materials and in creating new materials. In this chapter, we first focus on the ancients' speculation of *atoms*. The early concept of atoms was produced by some ancient Greek philosophers. Although it took humans more than two thousand years to establish the concept of crystals from the age of the ancient Greeks, the idea of geometrical packing of small building blocks (atoms, molecules, or unit cells in modern science) is supposed to have been somewhere in the humans' consideration. After explaining crystals as one of the most fundamental forms of materials, we will show *quantum materials* and *pattern formation* as the fields with which mathematics has a strong relationship.

**Keywords** Crystallography · Aperiodic system · Standard realization · Band theory · Quantum Hall effect · Topological insulator · Pattern formation · Crystal growth · Reaction-diffusion equation

## 2.1 Geometric Structures of Atomic Configurations

### 2.1.1 Atomism

The first interaction between mathematics and materials is possibly seen in the concept “atomism.” In Ancient Greece (5th–4th century BCE), philosophers Leucippus, Democritus, and Epicurus, proposed their two principles of atom and void. They theorized that there exists an ultimate small particle that cannot be divided any further. Naturally, at the time, it was impossible to prove this idea and therefore their atoms remained imaginary. However, it is amazing that they conceived the idea of atoms

**Fig. 2.1** Five Platonic solids (polyhedra) drawn by Johannes Kepler in his work “*Harmonice Mundi* (1619).” Octahedron, tetrahedron, dodecahedron, cube, and icosahedron were associated with air, fire, the universe, earth, and water, respectively

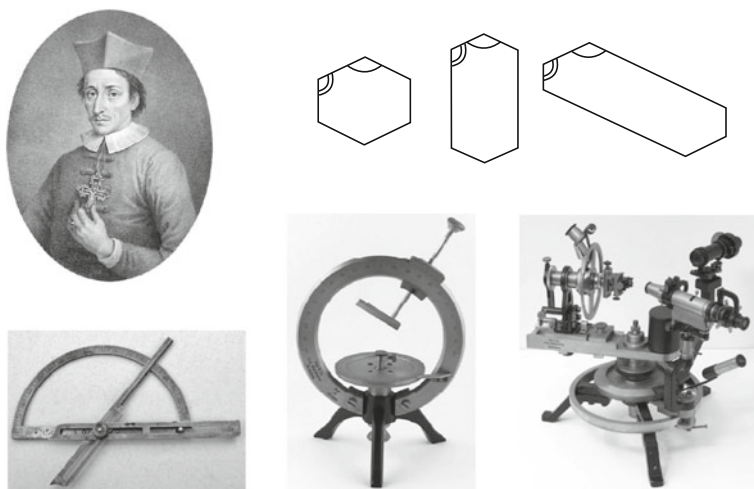


about 2,500 years ago. The ancient Greek philosophers were also mathematicians and therefore it is possible that they thought matter could have a mathematical basis. Democritus likewise said “*All matter is made from invisible atoms like blocks which cannot be separated any more. The universe consists of countless atoms of different shape, size, arrangement and location, and an atom is classified by emptiness.*” He believed that real objects can exist because of the existence of emptiness which allows the objects to move without obstruction. Although Plato is not recognized as an “atomist,” he developed his own idea of atoms based on geometric objects. He argued that all of creation is made up of five polyhedra (elements): octahedron (air), tetrahedron (fire), dodecahedron (the universe), cube (earth), and icosahedron (water); see Fig. 2.1. He believed all things are made up of an unchanging level of reality based on mathematics. These fundamental polyhedra cannot be divided into smaller parts because they would lose their beauty if they collided with another (e.g., [Cro]).

Unfortunately, this ancient form of atomism was forgotten for more than 2000 years before modern atomism was proposed by John Dalton in the early 1800s. Moreover, more trustworthy evidence for the existence of atoms was presented 100 years later in the theory of Brownian motion proposed by Albert Einstein in 1905 and the diffraction of X-rays by crystal lattices in the early 1910s by Max von Laue, William Henry Bragg and William Lawrence Bragg. W. L. Bragg developed the new technique to calculate atomic arrangements in crystals and this discovery depended largely on his ability in mathematics. Later, with transmission electron microscopes and scanning tunneling microscopes, researchers began at last to observe atoms directly.

### ***2.1.2 The Miracle Year of 1669; The Emergence of Crystallography and Optocrystallography from Mineralogy***

In physics, the year 1905 is often called the “miracle year” because Albert Einstein published three important papers, the theory of the photoelectric effect based on the quanta-of-light hypothesis, the theory of Brownian motion, and the special theory of relativity. Here, we describe another “miracle year,” which initiated the science of



**Fig. 2.2** A portrait of Nicolaus Steno (from Wikimedia Commons), the law of constant angle, and development of the goniometer for measuring interplanar angles. Photos of goniometers from the collection at the Virtual Museum of the History of Mineralogy (<http://www.mineralogy.eu/index.html>) are reproduced here with the museum's kind permission

crystals. Nicolas Steno (1638–86), a Danish scientist of the 17th century, discovered the “law of constant angle” in 1669 (Fig. 2.2). The law stipulates that the interplanar angle formed by two crystal faces (e.g., the angle formed by the (100) plane and (111) plane) are universally constant for the same kind of crystal (mineral). Based on this law, Steno reached the conclusion that crystals grow through the attachment of small particles to crystal facets and the rate of attachment (growth rate) differs for each facet (orientation of the crystal). We see in Steno’s discovery definite geometric considerations.

In 1669, another great discovery was achieved by another Danish scientist, Rasmus Bartholin (1625–98). He discovered the “double refraction” of light rays in calcite crystals (Fig. 2.3). This observation formed the basis of the optics of crystals. Before 1669, crystals were mysterious substances and it was beyond human understanding to find mechanisms underlying their fascinating properties. Although descriptive mineralogy existed and the classification of the many kinds of minerals (most minerals are crystals) had been almost completed, the real nature of minerals, for example, the reason why crystals are surrounded by facets, was still unclear. After 1669, however, crystals became a matter for science. We believe that this miracle year, 1669, is the starting point of the modern science of minerals and crystals that subsequently led to materials science. Furthermore, as mentioned above, mathematics, in particular, geometry, played an important role in opening up the new world of materials-related science.

Incidentally, Steno produced another big discovery in 1669—the “law of superposition”—in the same book *“De solido intra solidum naturaliter contento*

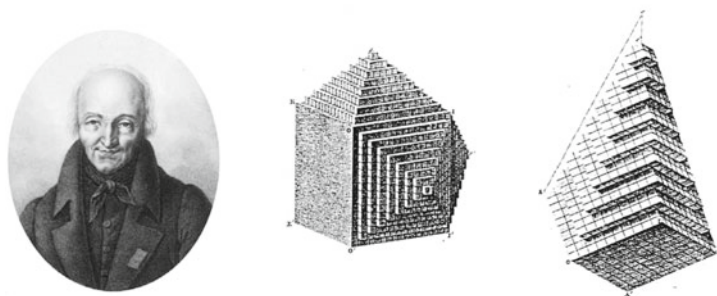


**Fig. 2.3** A portrait of Rasmus Bartholin (from Wikimedia Commons) and a calcite single crystal showing double refraction

*dissertationis prodromus*". However, this law is no longer mentioned here because the principle is only remotely related to materials science.

One hundred years after the Steno's discovery of the "law of constant angle", French mineralogist René-Just Haüy (1743–1822) discovered the "law of rational indices." This law states that the indices of any crystal faces are proportional to three small integers. This law also clearly indicates that crystals are composed of small repeating units (building blocks) each with the same shape and same size (Fig. 2.4). Moreover, it provided a microscopic basis for Steno's law showing that the fundamental forms of crystals lie in geometry.

Throughout the 19th century, the understanding of materials greatly progressed. In particular, the field of *crystallography* advanced considerably. For one, given that matter is composed of Daltonian atoms, their atomic arrangements are naturally expressed by *graphs*. A graph is a mathematical structure modeling the interaction (denoted by edges) between objects (vertices). In crystals, atoms are represented by the vertices and interactions by edges. Many materials scientists agree that one of the biggest contributions of mathematics to materials science is Group Theory.

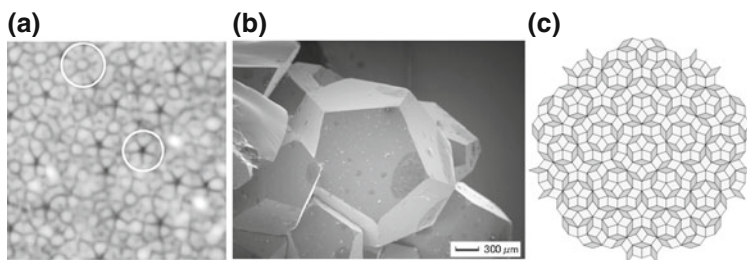


**Fig. 2.4** A portrait of René-Just Haüy (from Wikimedia Commons) and his model of a crystal consisting of small building blocks with the same shape and same size. Reproduced from "Traité de Minéralogie (1801)"

The concept of group is a mathematical means to describe the regularities, i.e., point symmetries and periodicities (translation symmetries), inherent in the atomic arrangements (lattices) in crystals. The concept began with Évariste Galois and later extended to the notion of continuous transformation groups by Marius Sophus Lie. Mathematicians played a central role in providing the classification of the 230 space groups belonging to three-dimensional space. This proof was independently established by E.S. Fedorov in 1890, A.M. Schoenflies in 1891, and W. Barlow in 1894. Clearly, mathematics is contributing significantly to the development of materials science through the structural analysis of crystals.

### 2.1.3 Quasicrystals

In 1982, Daniel Shechtman observed pentagonal symmetry in the electron diffraction pattern (Bragg diffraction) of an aluminum alloy sample using a transmission electron microscope and discovered the existence of quasicrystals [SBGC]. One example of a quasicrystal structure is shown in Fig. 2.5a. All crystals have translational symmetry and hence, by a mathematical principle, pentagonal symmetry is prohibited for crystal structures. Thus, the discovery of pentagonal symmetry surprised many researchers and there were heated discussions on whether quasicrystals were a new type of material or some subspecies of crystals involving twinning or unstable intermediate phases. Through the efforts of An-Pang Tsai, many stable quasicrystals were successfully synthesized (e.g., [TIM]; Fig. 2.5b), and quasicrystals attained independent status as a new category of materials. Discovery of these quasicrystals brought about a paradigm shift. Specifically, before their discovery, there were only two classes from the viewpoint of atomic arrangement; one is materials having long-range periodic order and the other is materials having a *random* structure. After the discovery, researchers recognized that long range order does not necessarily mean the



**Fig. 2.5** **a** Scanning tunneling microscopy image (10 nm × 10 nm) showing the fivefold surface of the icosahedral i-Al-Pd-Mn quasicrystal, reproduced from [MSSL] with permission of the Royal Society. **b** A secondary electron image of a Zn-Mg-Dy quasicrystal obtained by scanning electron microscopy, courtesy of Prof. An-Pang Tsai, Tohoku University. **c** One example of a Penrose tiling (from Wikimedia Commons)

existence of translational symmetry, but can involve highly ordered atomic arrangements. Strictly speaking, mathematics did not directly contribute to this discovery. Before the discovery, however, the mathematics community had studied aperiodic tiling. In particular, in 1974, Roger Penrose [Pen] had discovered the so-called “Penrose tiling” (Fig. 2.5c) which is the structure corresponding to the atomic structures of pentagonal quasicrystals. Alan L. Mackay, a crystallographer, who proposed Mackay icosahedra in 1962 [Mac62], predicted in 1981 [Mac81] the possibility of forming quasicrystals associated with the Penrose tiling [Mac82]. More importantly, such tilings suggest where the higher order in quasicrystals originates. De Bruijn [deB] later proved this mathematically by the so-called *cut-projection method*. More specifically, it is an irrational projection of a part (or cut) of the 5-dimensional hyper-cubic lattice projected into a 2-dimensional space. In a sense, mathematics had predicted the possible existence of quasilattices before Shechtman’s discovery, but not a physical realization in terms of quasicrystals. This gives an important lesson for both mathematicians and materials scientists. Mathematics has great potential to predict new physical structures of materials and based on these mathematical predictions, materials scientists have good motivation to seek and synthesize some of them. The concept of quasicrystals provides strong support for mathematics–materials science collaboration.

In 1992, a new definition of “crystal” was given by the International Union of Crystallography as “materials whose atomic configuration shows sharp Bragg diffraction peaks and crystals include both ordinary periodic crystals and quasicrystals.” [IUC] Hence, quasicrystals fall within the definition from the perspective of point symmetries of the Bragg peaks.

### 2.1.4 Aperiodic Tiling and Disordered System

A natural mathematical question is to identify the atomic arrangements that admit sharp diffraction peaks. Good references for this subsection are [Sen] and [Ba] as well as references therein.

A mathematical model for the atomic arrangement of disordered materials is a *Delone set*, which is a set of points in a given  $\mathbb{R}^n$  satisfying *uniform discreteness* and *relative denseness*. We often consider the corresponding pure point measure (more precisely the autocorrelation measure) of a given Delone set instead of the set itself, and take the Fourier transform of the measure, which provides the mathematical definition of Bragg diffraction for the atomic arrangement. When the Fourier transform has pure discrete measures, the atomic arrangement is called a crystal according to the definition of the International Union of Crystallography. It is an easy consequence of Poisson’s summation formula that the atomic arrangement of a classical crystal satisfies the condition.

### X-ray diffraction

X-ray diffraction (XRD) is one of the most important analytical techniques in materials science. XRD enables us to determine the crystal structures (arrangement of atoms) and gives useful information about the structure of amorphous materials. In 1912, based on the latest scientific knowledge at that time, Max von Laue conceived the idea that X-rays would be diffracted by crystal lattices because the wavelengths of X-rays are almost the same as the size of unit cells of crystal lattices. Walter Friedrich (research associate) and Paul Knipping (graduate student) proposed an experiment to verify von Laue's intuitive idea and discovered the diffraction of X-rays by crystals. After their discovery, William Lawrence Bragg and his father William Henry Bragg began using the XRD phenomenon to investigate the atomic arrangements in materials and established a fundamental technique to determine the crystal structure of materials. To this day, Bragg's law,  $2d \sin \theta = n\lambda$ , is still used as one of the most fundamental equations in the analysis of crystal structures. (In the formula,  $d$  is the spacing between periodic crystal planes,  $\theta$  the angle formed by the X-ray beam and the crystal plane,  $\lambda$  the wavelength of the X-rays, and  $n$  an integer.) Diffraction takes place only when these parameters satisfy this equation.

Around 1948, about 35 years after his early work, William Lawrence Bragg, as director of Cavendish Laboratory at Cambridge, became interested in the structure of biological substances such as proteins. This period at the Cavendish Laboratory became truly famous when in 1953 James D. Watson and Francis H.C. Crick discovered the double helix structure of DNA. This discovery was based on XRD data and the basic biological fact that the amounts of adenine (A) and thymine (T), as well as the amounts of guanine (G) and cytosine (C), are the same. The story hidden behind this glorious discovery is well-known and presented in many books and documentaries. Although there are various opinions on this matter, it has been mentioned that Maurice H.F. Wilkins (awarded the Nobel Prize in Physiology for Medicine jointly with Watson and Crick in 1962) at King's College showed XRD photographs of DNA that Rosalind E. Franklin had taken to Watson and Crick. Franklin died young in 1958 and therefore was ineligible to receive the Nobel Prize although it was she who had taken the crucial XRD photographs of DNA. Moreover, in 1962, John C. Kendrew and Max F. Perutz of the Cavendish Laboratory were awarded the Nobel Prize in Chemistry for their work using XRD to elucidate the structure of proteins.

XRD is an old but still cutting-edge technology that continually contributes to new discoveries in materials and bio-materials science, even more than 100 years after its development [[Sci](#), [Nat](#)].

To this point, we have treated atomic arrangements (point sets) and *tilings* (partitions of the space  $\mathbb{R}^n$ ) interchangeably because there is a geometric correspondence between them. For a given atomic arrangement, we can construct Voronoi cells or dual Delone cells to obtain a tiling, and conversely we can construct an atomic arrangement from a given tiling by taking a representative point in each cell. This correspondence enables theorems from tiling theory to be applied to the study of



materials. The Penrose tiling is an example of an aperiodic tiling. To generalize the new notion of crystal, we apply the above to a disordered system. We view an atomic arrangement or a tiling as a dynamical system, as a pair of compact metric spaces (a completion of the metric space by all translations of the atomic arrangements or the tiling) and the action of  $\mathbb{R}^n$  as translations. The  $C^*$ -algebra and its  $K$ -theory is a useful tool to develop quantum mechanics on tilings or their corresponding atomic arrangements. This approach was initiated by Jean Bellissard, Johannes Kellendonk, Ian F. Putnam and their followers [Bel86, Kel, KP].

### 2.1.5 Graph Modeling for Nano-Materials

When one considers interactions between atoms, a *graph theory* is a natural choice of a mathematical structure to describe their relations. A graph consists of a pair of sets, one of vertices and another of edges, which represent atoms and bonding, respectively.

Following the Nobel Prize-recognized discoveries of graphene [Gei, Nov], fullerene [Osa, KHOCS], and the revolutionary devices based on carbon nanotubes [Iij], the mathematical studies of possible carbon-networks and their spectral properties have been most intensive both among the chemistry community and the mathematics community. One attempt involves the spectral study of Schrödinger operators on such networks. Another involves more general graphs in the context of *quantum graph models* [BK, EKKST]. Instead of solving partial differential equations (PDE's) for 2-dimensional materials, one can solve and study spectral properties of the corresponding ordinary differential equations (ODE's) on a quantum graph (such as carbon nanotubes) with proper junction conditions. The mathematical modeling of photonic crystals has also progressed along many different paths [JMW, Kuc].

Study of carbon network is one of the more promising research areas. Our discussion of them is continued in Sect. 3.3.

### 2.1.6 Crystal Lattices and Their Standard Realizations

To study the relationship between microscopic structures in materials and macroscopic properties, *discrete geometric analysis*, i.e., the analysis on graphs, is useful. Let us introduce an example of the application of discrete geometric analysis on a crystal lattice. See [KS02, Su13] for details.

A *crystal lattice* is defined as an Abelian cover of a finite graph. Precisely stated, a crystal lattice is a topological network distinct from its arrangement in physical space (2-dimensional, 3-dimensional, or  $n$ -dimensional). A question posed by Toshikazu Sunada was whether there is a “standard arrangement” of a given crystal lattice. Kotani and Sunada [KS00, KS01] have proved that there always exists a unique standard arrangement, which is called the *standard realization*, and gives the most symmetric one of a given crystal lattice. For example, the standard realization of the  $\mathbb{Z}^2$ -lattices is the square lattice, of the triangular lattice is the regular triangular lattice, and of the hexagonal lattice is the regular hexagonal lattice.



Sunada further studied and classified all 3-dimensional crystal lattices having the strong isotropic property when the lattices are arranged in their standard realization. Only two structures arise; one is the atomic arrangement of the carbon network of diamond, and the other is the maximal Abelian cover of the K4 graph (K4 lattice) [Su08]. Actually, this structure has been known for almost 100 years to crystallographers and crystal chemists and for over 50 years to materials scientists and solid state physicists, by various names such as the Laves net by Heesch and Laves, Net 1 by A.F. Wells, and **srs** in the Reticular Chemistry Structural Resource, and  $Y^*$  in the International Tables for Crystallography (see [HCO] for a history of the discoveries). Nevertheless, from a geometric viewpoint, it is worth mentioning the structure in terms of a “diamond twin,” because it has caught the attention of materials scientists. Based on first-principle calculation, Sunada’s collaboration with materials scientists predicted the emergence of novel electronic properties for the carbon K4 network [IKNSKA].

Heat flow is a macroscopic feature within materials produced by the microscopic behavior of random walks of particles on an atomic arrangement. Indeed, we derived the heat equation describing its flow over the Euclidean plane by taking a parabolic scaling limit of the random walk on a square lattice. In [KS00], it has been shown that it is possible to generalize this idea to general crystal lattices only when the atomic configuration of the crystal lattice is given by the standard realization. The notion of standard realization has proved to be a natural framework to bridge microscopic structure and macroscopic properties by proposing stable structures of several materials, including Mackay-like carbon networks [TLNKK].

## 2.2 Quantum Materials

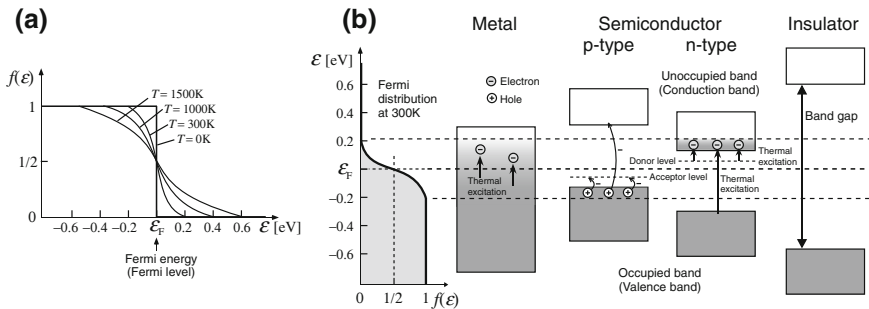
Quantum materials are materials with novel features and properties resulting from the quantum behavior of its electrons. They include, for example, superconductors, magnets, quantum-spin systems, multiferroic materials, as well as conventional semiconductors that have been the mainstay of modern electronics. We do not review the history of Quantum Mechanics throughout the 20th century, but recall that the electronic properties of periodic media (metals, semiconductors, and insulators) are now well understood in principle within “band theory” based on Bloch’s theorem. The spectrum and the band structure associated with the wave functions of an electron are obtained by specific Hamiltonians and the solutions of Schrödinger’s equation provided by an expansive mathematical knowledge of spectral analysis combined with Fourier calculus.

In real materials, there are many factors that break periodicity, such as impurities, defects, random perturbations because of environmental fluctuations, and the presence of magnetic fields. Hence, in recent studies of quantum materials, much emphasis has been placed on their topological properties. **Topology** is a mathematical tool to aid describing these properties, which display a strong robustness under continuous deformations. It is therefore natural to use  $K$ -theory, which studies the topological invariants of vector bundles of manifolds. A good survey for this section is [HK].

### 2.2.1 Electronic Characteristics of Periodic Materials System: Band Theory

Before discussing the hot topics of quantum materials, we begin by explaining the fundamental relationship between electronic structure and electrical properties of solids. As briefly stated in Chap. 1, Bloch's theorem is the basis from which to consider the behavior of electrons in periodic potentials in crystalline lattices. According to this theorem, the wave function (Eq. (1.3)) of an electron in a crystal is determined by wave vector  $\mathbf{k}$ , which determines the relational expression between energy and wave-number (the magnitude of the wave vector). Because of the scattering or diffraction of electrons resulting from a crystal potential with the translational symmetry of the lattice, Bragg diffraction, for example, produces some energy range forbidden to electrons. The states associated with these energies constitute the “forbidden bands” and the energy width is called the “band gap.” In contrast, because there is a large number of valence electrons in solids, the energy ranges excluding the forbidden bands, are filled with allowed energy states and form “allowed bands.” In this way, the quantum dynamics of the valence electrons is determined by the combination of allowed and forbidden bands, and the electronic characteristics of solids can therefore be roughly understood using band structure. Using “band theory,” the difference in properties of metals, semiconductors, and insulators can be clearly explained, as outlined in Fig. 2.6. In band theory, if the band just below the Fermi level (the valence band) is fully occupied by electrons and if the thermal energy is enough lower than the band gap energy, electrons cannot be excited to the unoccupied bands (conduction band). In this case, the material becomes an insulator, because all electrons in the occupied valence band cannot move. In metals, the Fermi level exists in an allowed band, and the electrons can be easily excited to higher energy states above the Fermi level and become mobile. The probability that an orbital at energy  $\varepsilon$  is occupied is expressed by the Fermi distribution function (Fermi-Dirac distribution function)

$$f(\varepsilon) = \frac{1}{\exp[(\varepsilon - \varepsilon_F)/k_B T] + 1}, \quad (2.1)$$



**Fig. 2.6** **a** Temperature dependence of the Fermi distribution function; **b** classification of metals, semiconductors, and insulators based on band theory

where  $\varepsilon_F$  is the Fermi energy (chemical potential of the system),  $k_B$  the Boltzmann constant and  $T$  the temperature [Kitt].

For semiconductors, the extent of this function is comparable to the band gap. Then, for n-type semiconductors, electrons in the donor states, as well as a small number of electrons in the valence band, can easily be excited into the conduction band and the material becomes conductive.

For a general introduction to semiconductors and spintronics, see **Appendix**.

### Superconductor

Superconductivity was discovered by Heike Kamerlingh Onnes in 1911. In 1908, he was the first to succeed in liquefying helium and thus opened a new research field of low temperature physics. In 1911, with the ability to cool materials, Onnes measured the temperature dependence of electric resistance of mercury. He observed a sudden drop in resistance down to zero when mercury was cooled to 4.2 K. He first thought it was caused by a short circuit, however, he finally understood that the resistance had really disappeared. Thereafter, although the transition temperature of superconductors,  $T_c$ , gradually increased, the study of superconductivity did not attract much attention for more than 70 years, despite being of interest to physics, because  $T_c$  was actually too low for practical use.

The breakthrough lay hidden in an unsuspecting corner. Johannes Georg Bednorz and Karl Alexander Müller at IBM Zurich Research Laboratory was interested in the relationship between the Jahn–Teller–type lattice distortion and superconductivity. In 1985, when they cooled the La-Ba-Cu-O perovskite, they observed a gradual decrease in resistance at 30 K that almost vanished at 10 K. This material was one kind of ceramics (in general, insulators) and for most researchers it was incredulous that this phenomenon was actually superconductivity. Since some unclear points remained in the experimental data to prove that their new material was a superconductor, Bednorz and Müller subsequently submitted the paper entitled “Possible high  $T_c$  superconductivity in the Ba-La-Cu-O system” [BM86, BM87].

Researchers at the Shoji Tanaka Laboratory at The University of Tokyo independently investigated this reported material and finally identified the superconducting phase from the mixture of compounds, thus confirming the first high-temperature superconductor. Historically, a “superconductor fever” followed this discovery. The Nobel Prize in Physics was awarded jointly to Bednorz and Müller in 1987, only 1 year after the publication of their paper.

The mechanism underlying high-temperature superconductivity of the copper oxides (cuprates) is still under debate because its  $T_c$  is much higher than that predicted by Bardeen–Cooper–Schrieffer (BCS) theory. Furthermore, a new superconductor series of iron pnictides, discovered by Hideo Hosono’s group at Tokyo Institute of Technology [KWHH], has furthered the mystery encountered with superconductivity. We certainly hope that mathematics rises to the challenge and solves this puzzle.

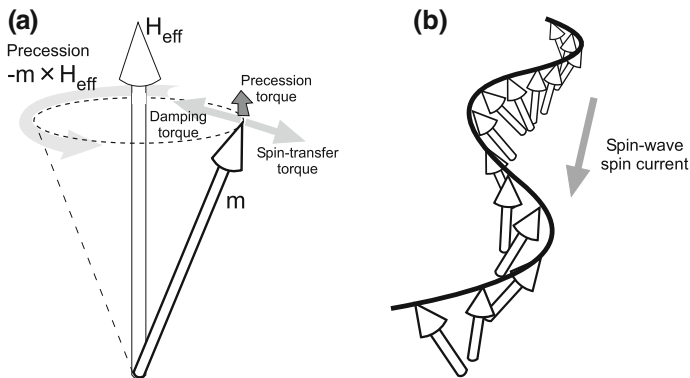
### 2.2.2 Spin Current

In the past one or two decades, the terminology “spin current” has gradually become one of the important keywords in spintronics. There are two kinds of spin current. One is the spin current accompanied by the flow of charge current; in this case, the current produces Joule heat. The other is spin current without a charge current; in this case, the spin current neither produces Joule heat nor energy dissipation.

We sometimes describe spin as if it has a single rigid direction. However, spin always exhibits a precessional motion (Fig. 2.7a), and this motion can be described by the Landau–Lifshitz–Gilbert–Slonczewski (LLGS) equation (e.g., [BKO])

$$\frac{\partial \mathbf{m}}{\partial t} = -\gamma \mathbf{m} \times \mathbf{H}_{\text{eff}} + \alpha \mathbf{m} \times \frac{\partial \mathbf{m}}{\partial t} + \boldsymbol{\tau}, \quad (2.2)$$

where  $\mathbf{m}$  is a unit vector along the magnetization direction,  $\gamma$  the gyromagnetic ratio,  $\mathbf{H}_{\text{eff}}$  the effective magnetic field, and  $\boldsymbol{\tau}$  the current-induced torques. In reality, a huge number of electrons coexist in a system, and one may picture them as many teetotums spinning, each teetotum exhibiting slow swinging (precessional) motion. Such a mass movement of spins actually occurs in ferromagnetic materials and in spin currents. In connection with this spin precession, a new spin current process has been discovered recently. In metals and semiconductors, a spin current is produced based on the migration of each electron having spin. However, in some magnetic insulators such as  $\text{Y}_3\text{Fe}_5\text{O}_{12}$ , Eiji Saitoh and his colleagues found that the spin-wave mode is a new form of conduction for the spin current [Kaj]. In this case, spin angular momentum can be carried by the collective magnetic moment precession without any migration of electrons (Fig. 2.7b). It is estimated that the spin-wave spin current can carry spin angular momentum up to several centimeters though the relaxation length of spin current is sub-micrometer at most. As well as these spin-wave spin currents, it is believed that a variety of phenomena remains to be discovered like a treasure box with big discoveries yet to be revealed even now.



**Fig. 2.7** a Precession expressed by the LLGS Eq. (2.2). b Spin-wave spin current [Kaj]

### 2.2.3 Integer Quantum Hall Effect (IQHE)

The IQHE was discovered by Klaus von Klitzing in 1980 (awarded the 1985 Nobel Prize in Physics). Conducted under a strong magnetic field and at low temperatures, it is a phenomenon in which the Hall conductance in a two-dimensional electron system is quantized, exhibiting discrete values  $\nu \times \frac{e^2}{h}$  with  $\nu \in \mathbb{Z}$ ,  $e$  electric charge and  $h$  Planck's constant [KDP].

Expressing the magnetic field  $B$  as a closed differential 2-form on a Riemann manifold, there exists a 4-vector potential  $A$ , which is a differential one-form satisfying  $dA = B$ . Then we have a connection  $\nabla_A = d + i\hbar A$  with which the magnetic Schrödinger operator is written

$$\frac{1}{2m} \nabla_A^* \nabla_A, \quad (2.3)$$

and acts on a line bundle on the manifold.

In 1982, D. Thouless, M. Kohmoto, M. Nightingale, and M. den Nijs [TKNN] shed further light on the IQHE from a geometrical viewpoint and introduced a topological invariant  $\nu$ , now called the *TKNN number*, corresponding to the Chern number of the  $U(1)$  bundle over the magnetic Brillouin zone.

As a consequence of this topological invariant, special edge states at the interface between two materials with different topological invariants are expected. These states were first identified by Bertrand I. Halperin [Hal] in 1982. Yasuhiro Hatsugai studied the Hall conductance of a system with edges, and defined the *edge index* as the winding number of the edge states on the Fermi surface. He then clarified the bulk–edge correspondence, the relationship between the edge index and the TKNN index (bulk index) [Hat]. The system with random potentials is treated in [BES].

### 2.2.4 Hofstadter's Butterfly

The tight-binding representation of the 2D electron under a uniform magnetic field acts on  $\mathbb{Z}^2$ . This situation is usually referred to as the Harper model [Hap];

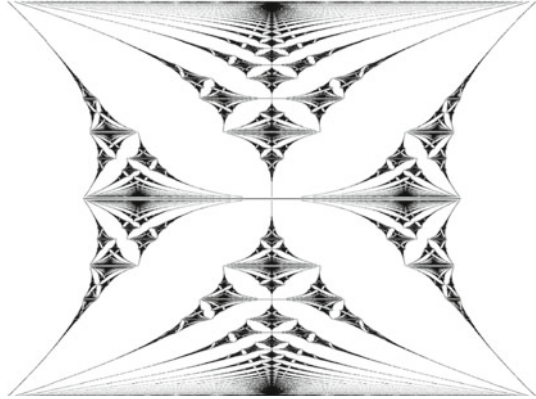
$$H = U + U^* + V + V^*, \quad (2.4)$$

where  $U$  and  $V$  are the so-called *magnetic translation operators*, which satisfy non-commutative relations

$$UV = e^{2i\pi\alpha} VU, \quad (2.5)$$

for the flux per unit cell of the lattice  $\mathbb{Z}^2$ .

**Fig. 2.8** Hofstadter's butterfly. Reprinted figure with permission from [Hof] (<http://dx.doi.org/10.1103/PhysRevB.14.2239>). Copyright (1976) by the American Physical Society



In 1976, Douglas G. Hofstadter [Hof] revealed its fractal nature as the magnetic field changes. This figure is now known as the Hofstadter butterfly (Fig. 2.8), and attracted much interest in mathematical physics. The *Ten Martini Problems* were posed by Barry Simon, so named after an offer of a martini for each solution by Marc Kac. In 1981, Kac conjectured that the spectrum of the Harper operator is a Cantor set for all irrational  $\alpha$ . The problem was solved affirmatively by Artur Avila and Svetlana Jitomirskaya [AJ]. Avila received the Fields Medal for the work.

The Lipschitz continuity of the edge of spectrum in  $\alpha$  was proved [Bel94] and generalized for general crystal lattices [Kot03].

Hofstadter's butterfly displays interesting geometric features such as point symmetry and self-similarity. If we consider phenomena encountered in a 2D space subjected to a magnetic field which is parameterized by  $\alpha$ , then it becomes difficult to explain. However, if we take the Harper operator as the Laplacian of the 2D non-commutative space where the right/left shift  $U/U^*$  and the up/down shift  $V/V^*$  are non-commutative, then the geometry of the Hofstadter's butterfly can be understood from an underlying non-commutative space. Non-commutative geometry is thus a natural framework to describe the phenomena.

### 2.2.5 Central Limit Theorem for Magnetic Transition Operators

The notion of magnetic transition operators was introduced by Toshikazu Sunada [Su94] as a generalized Harper operator. The Harper operator on  $\mathbb{Z}^2$  is a discretized magnetic Schrödinger operator on  $\mathbb{R}^2$ , but the magnetic transition operators

are defined on an abstract crystal lattice. Because magnetic fields are differential 2-forms, there is no trivial counterpart on a graph. Sunada used the group cohomology  $H^2(\mathbb{Z}^d, \mathbb{R})$  as a substitute of magnetic fields (more precisely a magnetic flux class over the unit cell) and defined a family of magnetic transition operators parameterized by  $H^2(\mathbb{Z}^d, \mathbb{R})$ . To show the notion is a good discrete analogue, a central limit theorem has been established in [Kot02] forming a bridge between the discrete and continuum. The magnetic Schrödinger operator in  $\mathbb{R}^d$  was identified as the scaling limit of the magnetic transition operator.

### 2.2.6 Topological Insulator

Undeniably, electronics is one of the basic technologies of the modern age. However, instead of using electric currents, we can consider exploiting spin currents by replacing electric charges with spins. The new technology to generate and control spin current is called “spintronics” (details of this topic will be given in Appendix).

In 2004, S. Murakami, N. Nagaosa, and S.C. Zhang predicted spin currents in *spin Hall insulators* [MNZ04]. Because such materials are expected in theory to have no electric current and therefore no energy dissipation, this feature indicates a big potential for applications of spintronics (Fig. 2.9).

In 2005, Charles. L. Kane and Eugene J. Mele [KM] theoretically predicted a *quantum spin Hall effect* for 2D systems with spin up and down electron and time-reversal symmetry (Bernevig, Hughes, and Zhang [BerHZ]); Fu and Kane [FK] in 2006, and independently J. Moore and L. Balents [MB] in 2007, predicted the same for 3D systems. They were confirmed experimentally by L. Molenkamp et al. [Kön] for the 2D case in 2007, and by M. Hasan et al. [Hsi] for the 3D case in 2008. The

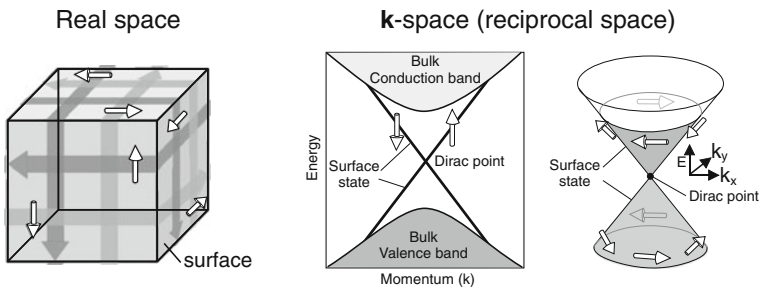


Fig. 2.9 Schematic of a band dispersion for topological insulators



$\begin{smallmatrix} d \\ \text{class} \end{smallmatrix}$	0	1	2	3	4	5	6	7	T	C	S
A	$\mathbb{Z}$	0	$\mathbb{Z}$	0	$\mathbb{Z}$	0	$\mathbb{Z}$	0	0	0	0
AIII	0	$\mathbb{Z}$	0	$\mathbb{Z}$	0	$\mathbb{Z}$	0	$\mathbb{Z}$	0	0	1
AI	$\mathbb{Z}$	0	0	0	$2\mathbb{Z}$	0	$\mathbb{Z}_2$	$\mathbb{Z}_2$	+	0	0
BDI	$\mathbb{Z}_2$	$\mathbb{Z}$	0	0	0	$2\mathbb{Z}$	0	$\mathbb{Z}_2$	+	+	1
D	$\mathbb{Z}_2$	$\mathbb{Z}_2$	$\mathbb{Z}$	0	0	0	$2\mathbb{Z}$	0	0	+	0
DIII	0	$\mathbb{Z}_2$	$\mathbb{Z}_2$	$\mathbb{Z}$	0	0	0	$2\mathbb{Z}$	-	+	1
AII	$2\mathbb{Z}$	0	$\mathbb{Z}_2$	$\mathbb{Z}_2$	$\mathbb{Z}$	0	0	0	-	0	0
CII	0	$2\mathbb{Z}$	0	$\mathbb{Z}_2$	$\mathbb{Z}_2$	$\mathbb{Z}$	0	0	-	-	1
C	0	0	$2\mathbb{Z}$	0	$\mathbb{Z}_2$	$\mathbb{Z}_2$	$\mathbb{Z}$	0	0	-	0
CI	0	0	0	$2\mathbb{Z}$	0	$\mathbb{Z}_2$	$\mathbb{Z}_2$	$\mathbb{Z}$	+	-	1

**Fig. 2.10** Periodic table of topological insulators and superconductors. [RT]

materials exhibiting the effect are referred to as *topological insulators (TIs)* because they have conducting states (associated with a spin-polarized Dirac fermion) on the boundary (edge or surface) topologically protected as well as a bulk band gap like ordinary insulators. Other phenomena such as the topological magnetoelectric effect and zero-resistivity in topological superconductors (TSCs) were also found.

The discovery of TI and TSC, and their expression using the more general notion of *topological quantum numbers*, nicely fits in the  $K$ -theory framework. A classification of TI and TSC has been given in terms of a symmetry known as the Bott periodicity [AZ, Kita], which gives a one-one correspondence between D-brane charges and the periodic table for topological insulators and superconductors (Fig. 2.10).

### 2.2.7 Non Commutative Bloch Theory

Let us now consider the quantum mechanics for aperiodic media as an application of  $K$ -theory of the  $C^*$  algebra. This idea was pioneered by Jean Bellissard [Bel86] using the framework of non-commutative geometry, which was created by Alain Connes [Con]. He received the Fields Medal in 1982 for his work. Non-commutativity has been used to explain the quantization of the quantum Hall conductivities and

gap labeling. It is viewed as a promising mathematical framework for quantum mechanics, called *non-commutative Bloch theory* for aperiodic media in general, including periodic media with impurities or defect, quasicrystals, glassy materials, and amorphous materials (cf. [BHZ, KP]).

Using the framework, one derives a bulk–edge correspondence for the IQHE with random potentials [KRS, KSV]. Recently, the notion of *gap index* has been introduced and used to show the bulk–edge correspondence is equivalent to push-forwards via the Gysin map [FHKMS]. Yasuhiro Kubota has established a general framework for the bulk–edge correspondence of non-periodic Hamiltonians associated with disorder systems using coarse geometry and classified in terms of the K-group of the Roe algebra [Kub].

## 2.3 Pattern Formation

Generally, materials are created through some chemical reactions or phase transitions. The final products of these chemical reactions/phase transitions are basically determined by thermodynamics, that is, ensembles of materials (phases) in equilibrium appear as final products. However, the textures (e.g., shape of crystals) of the final products show a certain variation depending on the processes involved, including various non-equilibrium and/or non-linear elementary processes (reactions/transitions). Processes forming “patterns” are referred to as *pattern forming* processes, which also influence the properties of materials.

The *calculus of variations* was developed in the 17th–18th century initiated by Pierre-Louis Moreau de Maupertuis. Phenomena in nature are governed by “the law of least action” associated with *the laws of motion and of rest deduced from a metaphysical principle* (1746). The founding fathers of the calculus of variations were the brothers Johann and Jacob Bernoulli, and Johann’s student Leonhard Euler. Completion of its foundation was done by Joseph Louis Lagrange. Maupertuis’ vaguely formulated philosophy evolved into an elegant mathematical expression, called the *Euler–Lagrange equation* (cf. *Mécanique Analytique* (1788, J.L. Lagrange), and reformulated classical mechanics based on the *variational principles* by William R. Hamilton and Friedrich H. Jacobi.

We need mathematics to describe both spatial shapes in equilibrium and transition dynamics toward equilibrium from non-equilibrium states. We start this section with static pattern formation, which is determined by thermodynamic equilibrium, and gradually precede to dynamic processes such as crystal growth and reaction–diffusion processes. Afterwards, some mathematical ideas to deal with dynamic crystal growth processes, for example, *level set method* and *phase field method* will be described.

### 2.3.1 Patterns in Equilibrium: Soap Films, Soap Bubbles

Soap films and surfaces of biological or metallurgical cells, are governed by surface tension. Surfaces that model soap films minimize the surface tension energy are in mathematics called *minimal surfaces* with prescribed boundaries that satisfy the so-called *minimal surface equation* derived by Lagrange;

$$\frac{\partial}{\partial x} \left( \frac{f_x}{\sqrt{1 + f_x^2 + f_y^2}} \right) + \frac{\partial}{\partial y} \left( \frac{f_y}{\sqrt{1 + f_x^2 + f_y^2}} \right) = 0, \quad (2.6)$$

for a graph  $z = f(x, y)$ .

Historically, the experimental observations by Joseph A.F. Plateau (*Statique Expérimentale et Théorique des Liquides soumis aux Seules Forces Moléculaires* (Experimental and Theoretical Statics of Liquids Subjected Solely to Molecular Forces) published in 1873 inspired mathematics considerably. The Fields medal was awarded to Jim Douglas and Tibor Radó for their solution of the “Plateau’s problem” (proving the existence and uniqueness of the minimal surfaces with prescribed boundaries) in 1936.

The self-intersections (singularities) of soap films obey the following

**Theorem 2.1** (Intersecting Law) [Tay] *Minimal surfaces intersect over a line at 120 degrees (for three surfaces). Only four such lines can meet at a single point (bringing six surfaces together with the same angles between any two adjacent surfaces).*

It was also conjectured by Plateau and proved by Jean Taylor employing geometric measure theory (developed by Frederick J. Almgren Jr. and many other contributors). The theory gives a complete classification of the local structure of singularities of minimal surfaces. H.A. Schwarz discovered three examples of periodic minimal surfaces; *Schwarz D*, *Schwarz P* and the *Gyroid*. These surfaces appeared as interfaces in phase separations on various occasions in materials science.

Similarly, minimizing surfaces that confine a fixed volume such as soap bubbles, cells, and grain boundaries, cracks of materials, and crevasses in ice are important. They are called *surfaces with constant mean curvature* or *CMC* surfaces in mathematics and give mathematical models of interfaces of two different states: namely *bi-continuous* fields.

Stephen T. Hyde and his collaborators conducted a systematic study of bi-continuous or *poly-continuous* structures of such interfaces in nano-porous materials using minimal/CMC surface theory [HCO, HOP, HO, HR]. Bi-continuous

structures have been observed in mesoporous materials, and tri-continuous structures were first synthesized as interwoven porous channels in mesoporous silica by J. Ying et al. [HYZ].

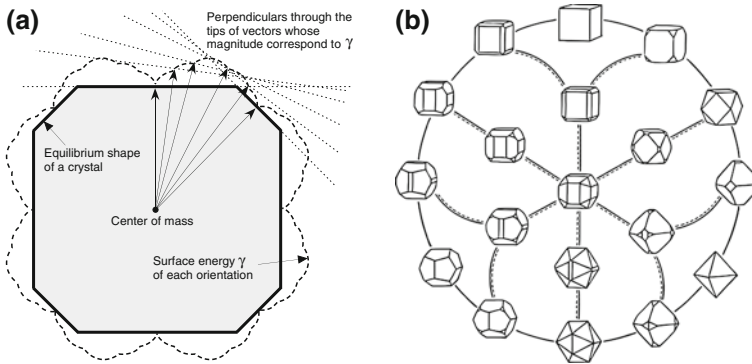
### 2.3.2 Fundamentals of Crystal Growth

Crystal growth is one of the more important physical and chemical processes in materials science because most of materials is made up of crystals (e.g., [Nis]). Generally, crystals grow from melts, solutions, or vapor phases, and most of the crystals pass through a nucleation process as an initial step in growth. In exceptional situations, some crystals are formed through phase transformations without nucleation such as spinodal decomposition. If we assume that small clusters of radius  $r$  are formed in supersaturated vapor or solutions, or supercooled melts, the change in free energy for the formation of the clusters can be expressed as

$$\Delta G(r) = -\frac{4\pi r^3}{3v} \Delta\mu + 4\pi r^2 \gamma, \quad (2.7)$$

where  $v$  is the volume of one atom/molecule,  $\Delta\mu$  the change in free energy of the system per atom/molecule, and  $\gamma$  the density of the surface energy. The first two terms originate from the volume and surface area of the clusters. If the radius exceeds critical radius  $r_c$ , the increase in volume causes a decrease in free energy of the system and enhances the further capturing of atoms/molecules (e.g. [Sun05]). This is the fundamental mechanism of *nucleation* and crystal growth follows after the nucleation. Crystal properties, such as size, shape, amount of impurities, and surface roughness, are largely influenced by the crystal growth process and the process is influenced by a kinetic condition depending on the degree of supersaturation and supercooling as well as a thermodynamic condition. For example, if the supersaturation/supercooling is small, the crystal growth rate is small and the shape of the crystals follows closely the equilibrium shape, which can be determined by the *Wulff construction* (e.g. [Lu]) as shown in Fig. 2.11a. In contrast, if supersaturation/supercooling is large, the growth rate is large and the shape differs from the equilibrium shape. For example, natural pyrite crystals show various shapes depending on the grown environments (Fig. 2.11b). Under larger supersaturation/supercooling conditions, crystals tend to take up more impurities from their environments changing their physical and chemical characteristics considerably.

We shall discuss topics related to crystal growth in several parts of this book because crystal growth is a key issue, which combines microscopic processes of materials and their macroscopic properties and features.



**Fig. 2.11** **a** An example of a Wulff construction. **b** Variations in crystal habit of pyrite [Sun57, Sun05]. Reproduced from [Sun57] with permission of Geological Survey of Japan, AIST

R.L. Dobrushin, R. Kotecký, and S. Shlosman [DKS] proposed in 1989 a microscopic description that uses the Ising model and showed that the Wulff construction appears as a scaling limit. The bridge between microscopic random behaviors of many interacting particles and macroscopic non-equilibrium dynamics of surfaces/interfaces is now studied intensively as the *hydrodynamic limit*. This notion originated with Charles B. Morrey [Mor] (cf. [KL]).

Named after its proposers Mehran Kardar, Giorgio Parisi, and Yi-Cheng Zhang in 1986, the KPZ equation describes the motion of growing interfaces [KZ]. More precisely, this equation is the non-linear stochastic PDE

$$\frac{\partial h}{\partial t}(x, t) = \nu \nabla^2 h(x, t) + \frac{\lambda}{2} (\nabla h)^2 + \eta(x, t), \quad (2.8)$$

where  $h$  is the height of the interface,  $\nu$  the surface tension, and  $\eta$  white noise (Gaussian), which describes the time evolution of the rough irregular interfaces between vacuum and accumulated material with white noise. The stochastic Burger's equation is a one-dimensional version of the KPZ equation. The combination of non-linearity and randomness causes highly singular behaviors of the solutions and makes a mathematically rigorous treatment of the KPZ equation difficult. Martin Hairer received the Fields medal in 2014 in establishing the theory of regularity structures as applied to the KPZ equation and a more general class of stochastic PDE [Hai].

After describing the diffusion and diffusion–reaction equations below, we shall consider problems of crystal growth again in relation to *mean curvature flow* and some methods describing pattern formation during crystal growth.

### Diffusion

Diffusion is a fundamental process in material transport and also important in materials science. From the macroscopic viewpoint, diffusion is a process that homogenizes the concentration; transport proceeds from a high to low region of concentration, and the distribution of concentration gradually becomes uniform. Strictly speaking, the driving force of diffusion is a difference in chemical potential, thus the gradients of temperature and electric potential, as well as concentration, can function as driving forces. Here, however, we consider diffusion as a phenomenon simply driven by a concentration gradient. The most basic formulation of diffusion is given by Fick's law, which in one dimension is expressed in the form

$$\frac{\partial u}{\partial t} = D \frac{\partial^2 u}{\partial x^2}, \quad (2.9)$$

where  $u$  is the concentration,  $t$  the elapsed time,  $x$  the space coordinate, and  $D$  the coefficient of diffusion without anisotropy.

Crank published the text book "The Mathematics of Diffusion" [Cra], which assembles and organizes the solutions of the diffusion equation solved under various boundary conditions. For example, if we assume that a thin-film diffusing source of total amount  $M$  exists at  $t = 0$ , the distribution of concentration at time  $t$  is given by

$$u = \frac{M}{2(\pi Dt)^{1/2}} \exp\left(-\frac{x^2}{4Dt}\right). \quad (2.10)$$

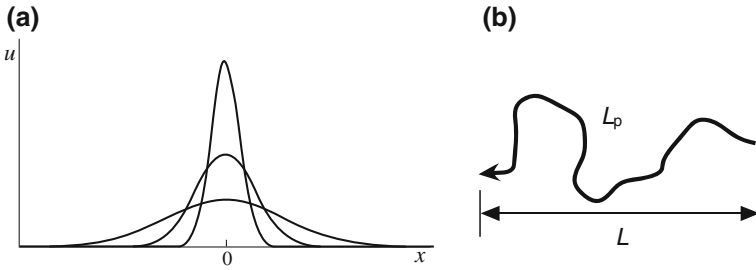
This distribution is shown in Fig. 2.12a.

In actual systems, for example in nanoporous media, diffusion is not so simple and the concept of "tortuosity" is used (e.g., [Nak]). Tortuosity  $\tau$  is defined as  $\tau = L_p/L$ , the ratio of the length of the curve  $L_p$  to the distance between its ends  $L$  (Fig. 2.12b). As  $\tau$  increases, material transport is suppressed. In this case, the apparent coefficient of diffusion is approximately expressed using tortuosity  $\tau$  as

$$D_{app} = \frac{D}{\tau^2}. \quad (2.11)$$

Diffusion occurs in every process involving materials and is an important essential in materials science.

One microscopic aspect of diffusion is the notion of random walks for the atoms. We can observe random walk of atoms by scanning tunneling microscopy and estimate the macroscopic diffusion coefficient (e.g., [MKWL, WCBET, MRPC]). How does the atomic arrangement determine macroscopic diffusions? It is a consequence of the *Central Limit Theorem*. The simple random walk of atoms on the square lattice with parabolic scaling converges to Brownian motion whose distribution law is given by (2.9) as the scaling goes to zero. The classical result was generalized to arbitrary crystal lattices using their standard realization [KS00].



**Fig. 2.12** **a** Time evolution of the concentration distribution based on the Eq.(2.10); **b** schematic of material transport through a complicated path

### 2.3.3 Reaction–Diffusion Equation

#### Turing Pattern

Alan Turing opened new insights into pattern formation in nature. In 1952, he claimed in his paper titled “The chemical basis of morphogenesis” [Tur] that pattern formation in biological systems is controlled by chemical reactions. The notion of *diffusion-driven instability*, namely, “non-uniformity may arise naturally out of a homogeneous, uniform state,” introduced by Turing, was surprising because the diffusion usually brings a homogeneous stable state. A certain system consisting of two chemical components with different coefficients of diffusion causes instability. Non-trivial patterns can arise in a homogeneous system as a result of competition between reaction and diffusion.

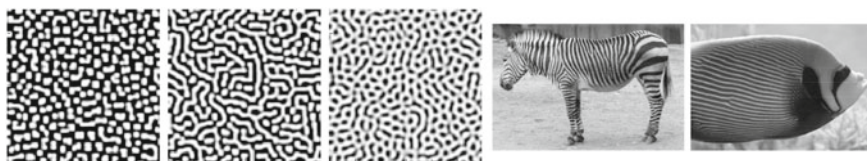
A basic set of the reaction–diffusion equations for such pattern formation is expressed as follows:

$$\begin{aligned}\frac{\partial u}{\partial t} &= f(u, v) + D_u \nabla^2 u \\ \frac{\partial v}{\partial t} &= g(u, v) + D_v \nabla^2 v,\end{aligned}\tag{2.12}$$

where  $u = u(r, t)$  and  $v = v(r, t)$  are concentrations of the two chemical components,  $D_u$  and  $D_v$  are the coefficients of diffusion of the two components, and  $f$  and  $g$  are chemical reaction rates.

If the coefficients of diffusion for two components are quite different and the reaction terms  $f$  and  $g$  satisfy some condition, these equations spontaneously produce characteristic patterns seen in nature, including patterns of some animals and fishes





**Fig. 2.13** Simulated Turing patterns and patterns seen on a zebra and an emperor angelfish. The first three simulated patterns are reproduced from Wikimedia Commons and the latter two photographs are from Pixabay

(Fig. 2.13). These patterns, which are known as *Turing Patterns*, originate from some instability depending on the delicate balance between reaction and diffusion.

### BZ Reaction

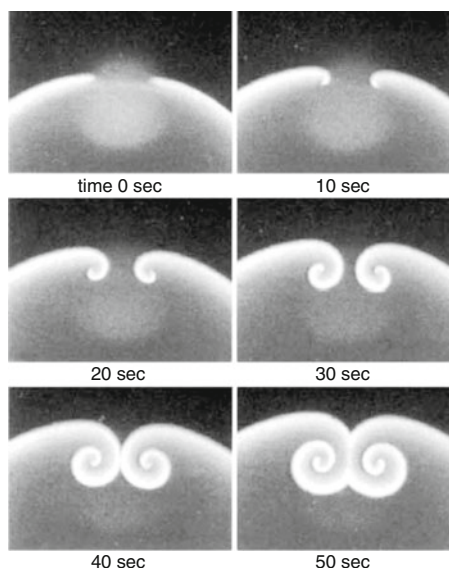
A biochemist Boris P. Belousov in 1958 [Bel] proposed a system with more than two components to explain an oscillating chemical reaction. This was confirmed experimentally by Anatol M. Zhabotinsky [Zha] and the equation became known as the *BZ (Belousov–Zhabotinsky) equation*. Rich patterns are generated under the same physical environment but slightly different initial conditions (Fig. 2.14).

A deep question is how patterns are formulated and how they are selected from several stable solutions of the equations. Little is known in general. It may be answered by looking at dynamical properties, hidden structural stabilities, and global attractors. A good reference for the following discussion is [N].

There are four classes of reaction–diffusion systems (Eq. (2.12)):

- Turing system,
- Oscillatory system,

**Fig. 2.14** Formation of an oscillatory spiral pattern from the BZ reaction. Courtesy of Dr. Tatsunari Sakurai (Chiba University) and Prof. Yasumasa Nishiura (Tohoku University)



- Excitable system,
- Bi-stable system,

depending on the dynamical nature of the corresponding kinetic equations  $u_t = f(u, v)$  and  $v_t = g(u, v)$ .

The bi-stable system has two attractors whereas the others have one. The oscillatory system has a limit cycle as its attractor. As we have already seen, the Turing system has a diffusion-driven instability; this occurs because the stable point of the kinetic equation is destabilized by the diffusion terms. The excitable systems exhibit the more interesting phenomenon such as the BZ reaction, Rayleigh–Bénard convection, and nematic liquid crystals.

### Cahn–Hilliard Equation

John W. Cahn and John E. Hilliard in 1958 [CH] proposed the following equation (Cahn–Hilliard equation), which is one of the basic reaction–diffusion equations and describes the process of phase separation such as spinodal decomposition:

$$\frac{\partial u}{\partial t} = D \nabla^2 (u^3 - u - \gamma \nabla^2 u) \quad (2.13)$$

where  $u$  is the concentration,  $D$  the coefficient of diffusion, and  $\gamma$  a parameter indicating the length of the transition regions between two kinds of domains. The two separated phases are expressed as  $u = 1$  and  $u = -1$ . In a spinodal decomposition, small fluctuations in the concentrations of mixed components gradually spread and domains of the two phases develop without nucleation (Fig. 2.15). There are variations of the *Allen–Cahn equation* [AC] and their stochastic versions.

### Far-From-Equilibrium Dynamics

Ilya Prigogine (Chemistry Nobel laureate in 1977) expanded Turing’s idea into a new broader field of science, called “dissipative structures.” A dissipative structure is a self-organizing structure, which appears in a dissipative system with steady-state going-in and out of energy. Such a state is achieved under far-from-equilibrium conditions [NP]. A typical example is any living organism such as our bodies. Our bodies are open systems, which take energy (foods) in and discharges heat and excretion. Inside bodies, there are some chemical reactions, which seem to oppose



**Fig. 2.15** Evolution of phase separation simulated based on the Cahn–Hilliard equation. Captured snapshots from Wikimedia Commons

thermodynamics. Nevertheless, our bodies regulate continually toward a steady state. Prigogine and his colleagues thought that these systems are among the patterns that appear under far-from-equilibrium conditions.

The relationship between structure and function and that between structure and process are key issues in materials science. Revolutionary functions often emerge from intricate structures, and those structures are created in manufacturing processes under far-from-equilibrium conditions such as rapid cooling. Examples can be seen in condensed matters like glasses, powders, foams, granular materials, dense colloidal materials, polymers, and various particular systems of different sizes. One can say that the invention of processing techniques for novel materials resulted from explorations of how we can control far-from-equilibrium dynamics and pattern formation. Far-from-equilibrium dynamics is ubiquitous [N]; it is not only found in materials science and condensed matter physics but also surfaces in challenging issues encountered in biology, chemistry, geoscience, meteorology, astronomy, and social sciences. The mathematical study of far-equilibrium dynamics has just begun.

### 2.3.4 *Mean Curvature Flow to Describe Crystal Growth*

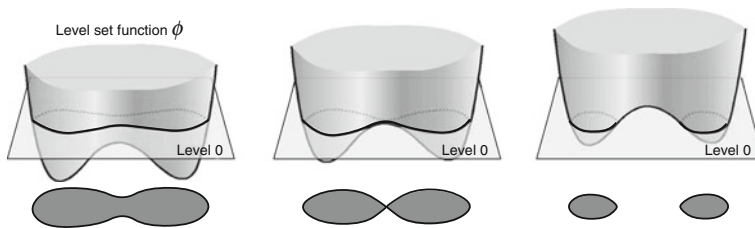
**Mean curvature flow** simply describes the movement of a curved plane for which the velocity along the normal direction is proportional to the mean curvature around each point on the surface. The concept of mean curvature flow was originally proposed in a model for the formation of grain boundaries in the annealing of pure metal by materials scientist William W. Mullins [Mul], and 20 years later Kenneth A. Brakke established a mathematically rigorous framework [Bra] (cf. [GG]).

Mathematically, the equation for mean curvature flow is difficult to solve because singularities appear in a finite time given smooth initial values. The **level set method** has been developed to overcome this difficulty. The idea first appeared in [OJK] and later introduced by Osher–Sethian in numerical calculations [OS].

Another approach to treat mean curvature flow is to use the “viscosity solution,” a generalized notion of classical solution of the PDE developed by Pierre-Louis Lions and Michael G. Crandall. In [CGG], the viscosity solution was proved to be useful in analyzing the mean curvature flow.

When we consider surfaces or interfaces with widths, the **phase field method** is efficient. The method introduces an auxiliary field that takes values 1 inside, gradually changing to -1 outside. Taking the scaling limit of the phase field equation, we obtain equations of the sharp surfaces and interfaces appearing in the Stefan model and Mullins–Sekerka model. The method provides models for needle-like crystals or dendritic crystals with side branches [Kob93, Kob94].

The following gives a brief introduction to the **level set method** and **phase field method**.



**Fig. 2.16** Schematic explaining the concept of level set method

### 2.3.5 Level Set Method

Stanley J. Osher (2014 Gauss Prize winner) and James A. Sethian developed “*level set method*” to compute moving fronts involving topological changes. In the level set method, the curved surface is regarded as a contour at level zero of a certain function  $\phi$  (Fig. 2.16), and the equation of motion of the contour is replaced by a PDE of  $\phi$ . This PDE can be solved using the viscosity solution method.

One of the successful examples of its application to materials science is the simulation of epitaxial growth of thin films. A simulation of crystal growth is often carried out as an atomistic process, for example, using the molecular dynamics (MD) method or Monte Carlo method. In such cases, the computation load is very high because it has to treat thousands of atoms individually. The level set method simulates only the boundary between the underlayer and overlayer and does not treat each atom. This simulation seems rough compared with other simulation methods using atomistic process. However, the method is based on rigorous mathematics and yields some benefits. Also, in comparison with results from other methods, the level set method has been proved to derive accurate results, for example, in the distribution of island sizes in epitaxial growth [CR].

### 2.3.6 Phase Field Method

If a solid/liquid interface moves during solidification (cooling), the following three main laws apply: (1) curvature effect (Gibbs–Thomson effect), (2) conservation law of substances and energy (Stefan condition), and (3) diffusion of heat and substances in solid and liquid driven by a temperature or concentration gradient. However, it is very difficult to solve its time evolution not only analytically but also numerically. The phase field method was developed to solve such a problem.

The basic phase field model describing solidification and melting is

$$\begin{aligned}\frac{\partial u}{\partial t} + \lambda \frac{\partial \phi}{\partial t} &= \nabla^2 u \\ \alpha \varepsilon^2 \frac{\partial \phi}{\partial t} &= \varepsilon^2 \nabla^2 \phi + f(\phi, u; \varepsilon),\end{aligned}\tag{2.14}$$

where  $\phi$  is the order parameter indicating solid or liquid ( $\phi = -1$  and  $1$  indicate solid and liquid, respectively). The characteristic difference from other models (e.g., Stefan's model) is that the phase field model deals with a solid/liquid interface having some thickness (a “diffuse interface” is one for which  $\phi$  ranges from  $-1$  to  $1$ ) whereas Stefan's model deals with the interface as a discontinuous sharp boundary. This means that the phase field method does not treat the interface precisely (i.e., the precise position of the interface, which changes from one moment to the next, does not need to be recorded). Hence, this method makes it possible to generate complicated structures such as dendrites.

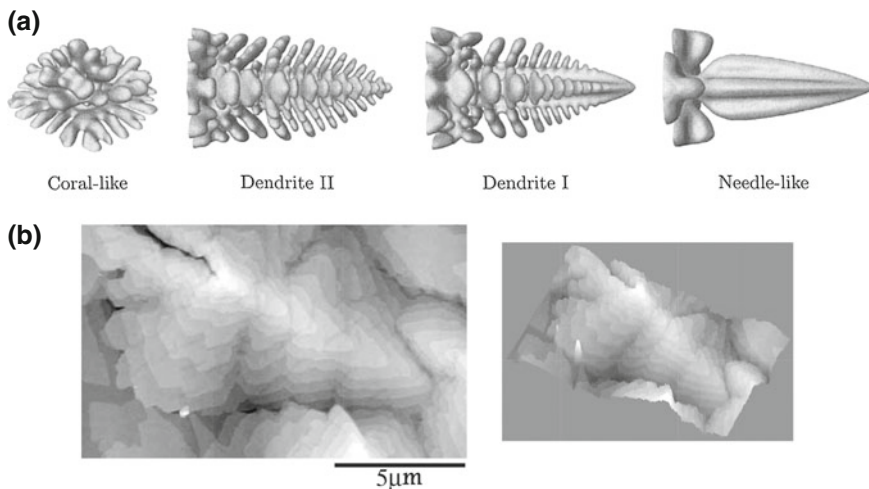
To simulate the growth of dendritic crystals, including the effect of anisotropy, Ryo Kobayashi [Kob94] used the following equations

$$\begin{aligned}\frac{\partial u}{\partial t} &= \nabla^2 u + \frac{\partial \phi}{\partial t} \\ \tau \frac{\partial \phi}{\partial t} &= \varepsilon^2 \nabla^2 \phi + \phi(1 - \phi) \left( \phi - \frac{1}{2} + m(T, -\nabla \phi) \right),\end{aligned}\tag{2.15}$$

$$\begin{aligned}m(T, v) &= -c \tan^{-1}(\gamma \sigma(v) T) \\ \sigma(\theta) &= 1 - \frac{1}{4} \delta (1 - \cos 4\theta)\end{aligned}\tag{2.16}$$

where  $\delta$  is a parameter controlling the degree of anisotropy. In changing its value from  $0$  to  $1$ , the pattern for the grown crystal changes from coral-like to needle-like via dendritic shapes (Fig. 2.17a). This morphological change can be seen in various materials systems. For example, organic semiconductor pentacene shows dendritic structure (Fig. 2.17b) if a thin film of pentacene is grown on an inert flat substrate (e.g.,  $\text{SiO}_2$ ) by molecular beam deposition method in vacuum.

These mathematical formulations for pattern formation have played an important role not only in understanding the pattern formation process but also in fostering ideas in controlling non-equilibrium and/or non-linear phenomena and designing structures of materials.



**Fig. 2.17** **a**  $\delta$ -dependence of the morphological variation using the phase field model. Reproduced from [Kob94] with permission from Taylor & Francis Group. **b** Topographic image obtained in atomic force microscopy of a thin film of the organic semiconductor *pentacene* grown on a silicon substrate with oxidized surface. The molecular steps for which the height almost corresponds to the length of a pentacene molecule (about 1.5 nm) are clearly seen. The 3D image was constructed by ImageJ software (U.S. National Institutes of Health; <http://imagej.nih.gov/ij/>). Please see [YTNK, PBNZ, SS] for the morphological variation of pentacene thin films

## 2.4 Other Tools

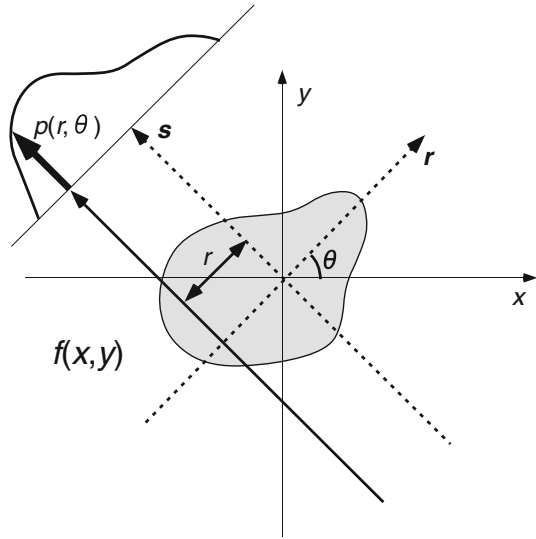
In this section, we introduce certain technologies, which are important in materials science, where mathematics plays a critical role in their realization.

### 2.4.1 Computed Tomography

Imaging techniques are crucial in the development of materials science. Nowadays, through their advancement, as with three-dimensional (3D) imaging, many important results have been accumulated regarding structure and formation of textures. X-ray computed tomography (CT) is one powerful technique used to observe 3D internal structures of materials. The fundamental principle in CT was given by Austrian mathematician Johann Radon in 1917. He invented the Radon transform which enables the reconstruction of 3D data from an infinite set of projections. The intensity of the transmitted X-ray through the object is

$$I = I_0 \exp \left( - \int \mu(x, y) ds \right), \quad (2.17)$$

**Fig. 2.18** Absorption of a parallel X-ray beam by an object



where  $I_0$  is the intensity of the incident beam and  $\mu(x, y)$  is the coefficient of attenuation for each point in the object (Fig. 2.18).

The intensity of the projection  $p(r, \theta)$  can be expressed using the Radon transform,

$$p(r, \theta) = - \int_{-\infty}^{\infty} \mu(r \cos \theta - s \sin \theta, r \sin \theta + s \cos \theta) ds \quad (2.18)$$

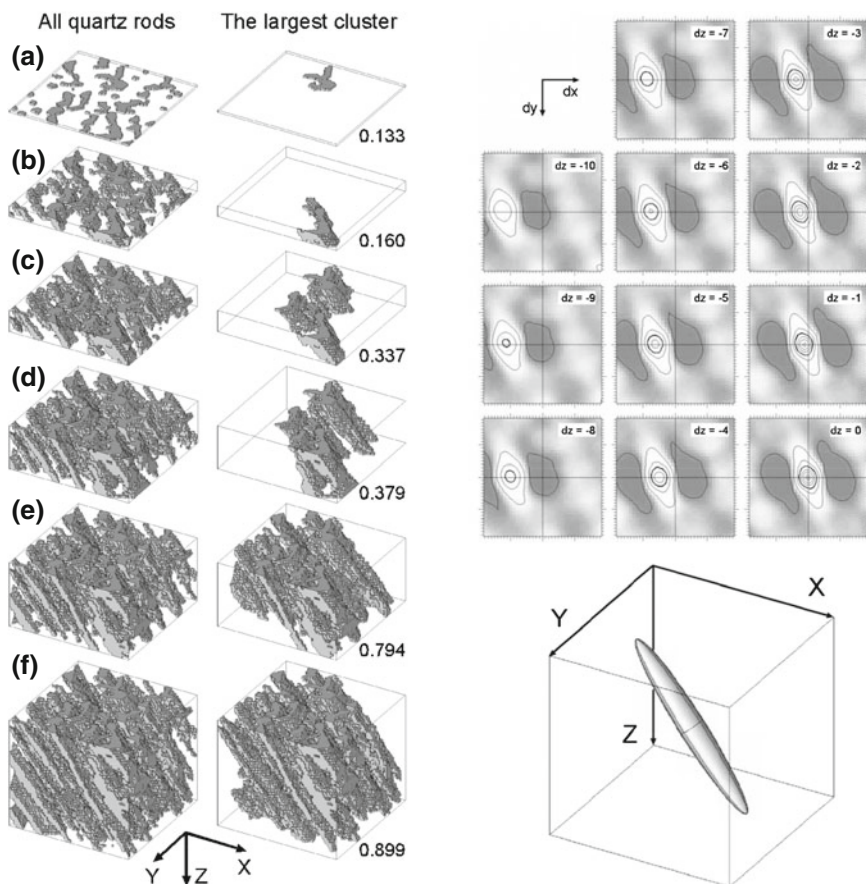
and coefficient of attenuation for each point  $\mu(x, y)$  can be obtained by the inverse Radon transform.

A computation technique for X-ray CT was first proposed by Allan M. Cormack in 1963 and 1964 [Cor63, Cor64]. He established the tomographic calculation procedure, which repeats the calculation to obtain discrete data using the Radon transform and its inverse. In 1971 (the paper was published in 1973), Godfrey N. Hounsfield succeeded in developing a practical X-ray CT scanner and obtaining tomographic images of the human brain based on Cormack's theory [Hou]. That few researchers were aware of Cormack's theory before Hounsfield's great invention of the century is a famous story.

An example of an X-ray CT image is shown in Fig. 2.19. X-ray CT involves non-destructive measurements enabling internal 3D structures to be obtained without damaging valuable samples. Such measurements are very important in medical diagnoses. The X-ray CT scanner exemplifies the successful industrial invention that is derived from the fruits of modern mathematics.

The field of X-ray CT is continuously making remarkable progress in the development of new mathematical algorithms. For example, for sparse image reconstruction from a limited number of projections and interior CT that can produce 3D images of





**Fig. 2.19** *Left:* An example of X-ray CT data showing the 3D connection of quartz crystals in natural graphic granite, and *Right:* Expression of the average 3D shape of quartz crystals using two-point correlation function  $AC(\delta) = \langle B(\mathbf{r} \cdot B(\mathbf{r} + \delta)) \rangle_{\mathbf{r}}$ . Republished with permission of the Mineralogical Society of Great Britain and Ireland, from [INN]; permission conveyed through Copyright Clearance Center, Inc

a region of interest (ROI) using limited projections of the ROI (e.g., [KCND, KSR]) as well as in the development of hardware.

### 2.4.2 Some Other Computational Tools

#### • Fast Fourier transform (FFT)

In spectral measurement in materials science, in particular, infrared spectral measurement, the FFT is indispensable enabling a frequency-absorption intensity

relationship to be obtained very quickly using white light without any monochromatized light and a spectroscopic mechanical system. The algorithm for the FFT was developed by American mathematicians, James W. Cooley and John W. Tukey, in 1965 [CT]. Strictly speaking, historical investigations suggest that Carl Friedrich Gauss had invented a similar algorithm around 1805. Nevertheless, they succeeded in decreasing the computational load dramatically by using the symmetry associated with the discrete Fourier transform (DFT).

Like X-ray CT, Fourier transform infrared (FTIR) spectroscopy is another very successful industrial invention based on the fruits of modern mathematics.

### • Nonlinear pattern fitting (peak separation)

In spectral analysis, we often face the overlapping of some peaks, for example, in X-ray diffraction measurement, and need to separate them into their individual components. In such situations, we apply nonlinear pattern fitting to separate peaks. In the computational procedure, we first have to decide the appropriate function that expresses the shape of the single peak. For example, the following normalized split (asymmetrical) pseudo-Voigt function, a combination of Gaussian and Lorentzian functions, is frequently used to fit to the shape of each peak (e.g., [Tor]):

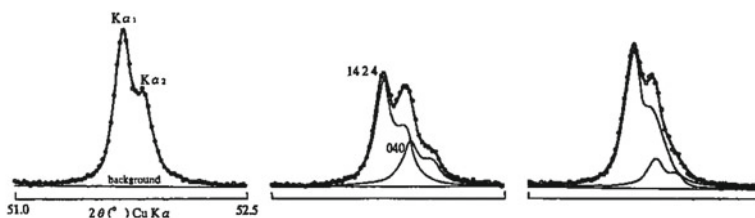
$$y(x) = I \frac{(1+A)\{\eta_{high} + (1-\eta_{high})(\pi \ln 2)^{1/2}\}}{\eta_{low} + (1-\eta_{low})(\pi \ln 2)^{1/2} + A[\eta_{high} + (1-\eta_{high})(\pi \ln 2)^{1/2}]} \times \left\{ \eta_{low} \frac{2}{\pi W} \left[ 1 + \left( \frac{1+A}{A} \right)^2 \left( \frac{x-T}{W} \right)^2 \right]^{-1} + (1-\eta_{low}) \frac{2}{W} \left( \frac{\ln 2}{\pi} \right)^{1/2} \exp \left[ - \left( \frac{1+A}{A} \right)^2 \ln 2 \left( \frac{x-T}{W} \right)^2 \right] \right\}, (x \leq T), \quad (2.19)$$

where  $I$  is the integrated intensity of the peak,  $T$  the peak position,  $W$  the full-width at half-maximum (FWHM) of a peak,  $\eta_{low}$  and  $\eta_{high}$  denote the ratio of the Lorentzian component at the lower and higher side of the peak, respectively, and  $A$  is another asymmetry parameter. Pattern fitting is essentially the process minimizing the sum of the squared residuals and the difference between the observed intensity at each position  $y(n)_{obs}$  and the calculated value  $y(n)_{calc}$  using the above function. First we calculate the partial differential coefficients with respect to  $I$ ,  $T$ ,  $W$ ,  $\eta_{high}$ ,  $\eta_{low}$ , and  $A$  for each position. (When the number of peaks is more than one, the treatment of the coefficients becomes slightly complicated.) All the partial differential coefficients become elements of a matrix  $A$  and the optimum values for parameters  $I$ ,  $T$ ,  $W$ , ... can be directly obtained by calculation with matrix equation

$$x = (A^T W A)^{-1} A^T W y, \quad (2.20)$$

where  $W$  denotes a weighting matrix.

For non-linear fitting, an iterative calculation (e.g., Gauss–Newton method) is necessary to find the best solution. Examples of X-ray pattern fitting [IJK94, IJK95] are shown in Fig. 2.20. Stable convergence is often difficult to achieve in iterative calculations and various mathematical algorithms, for example, the modified Marquardt method [Mar], have been proposed to guarantee a stable and rapid convergence. Recently, a novel method of spectral deconvolution based on



**Fig. 2.20** Some results of least-squares fitting of X-ray diffraction patterns reproduced from [IHK94]

Bayesian estimation with the exchange Monte Carlo method has been proposed to avoid a solution trapped in a local minimum because of system hierarchy and nonlinearity [NSO].

In Ancient Greece, there was no strict boundary between mathematics and other fields. Philosophers were mathematicians and meditated on anything from a deep mathematical perspective. Also in the early modern period, scientists, such as Isaac Newton, had all-around abilities and achieved great discoveries not only in mathematics but also in physics and chemistry. This implies mathematics is always central in all considerations. It is easy to imagine that mathematics or a mathematical perspective also influences materials-related sciences. A few centuries later, science has evolved into specialist fields. The wall between individual fields, especially between mathematics and other fields, is becoming wider and higher. Unlike Greek philosophers, there is no polymath with a broad knowledge of various fields. Of course, physicists use mathematics to describe theories and solve equations. However, in modern times, even physics seems to be developing independently of mathematics. In the past one or two decades, research institutions, departments, and governmental programs with aims to encourage interdisciplinary integration and create new scientific fields have been established. These attempts are based on the expectation that such meetings between different fields of knowledge will inspire new ideas not readily produced in a single-field environment with its limited knowledge and experiences. Even in physics, in which mathematics is in use every day, interactions with mathematicians will surely produce new ideas and findings.

In the following section, we shall discuss a recent trend in mathematics–materials science cooperation and collaboration. In just a few decades, it has been recognized that rationalizing design and development of materials is important as is the tightening of the development cycle by the creation of a predictive framework based on theory and mathematics. Various attempts have been proposed around the world to encourage the interaction of mathematics with other disciplines, as well as industry, to encourage innovation. A mathematics–materials science collaboration is one of those attempts.

## 2.5 Global Trend to Encourage Mathematics–Materials Science Cooperation

In the late 1990s, a movement emerged to promote interactions between mathematics and other fields of science and technology as well as industry. In 1998, the National Science Foundation (NSF) published what is often called the *Odom Report*. Its full title was “*Report of the Senior Assessment Panel for the International Assessment of the U.S. Mathematical Sciences*” and William E. Odom, Lieutenant General, USA (retired) was the chairman of the committee making the assessment. In this report, mathematical sciences were described as being traditionally active in Europe, but many talented mathematicians born in Europe were working in the US. As a consequence, the US had the strongest national community in the mathematical sciences in the world. This implied that US mathematics is strong but somewhat fragile. This report also noted that financial support going to mathematical sciences was lacking and there was some delay in promoting collaborations between mathematicians and users of mathematics similar to the leading-edge approach undertaken at the Isaac Newton Institute in the University of Cambridge. After the publication of this report, the NSF began actively encouraging interactions between mathematics and other disciplines with financial support. One typical example of the new direction can be seen in the Institute for Mathematics and its Applications (IMA) at the University of Minnesota. The IMA was established in 1982 with the objective of promoting synergies between mathematics and its applications. The NSF rated the IMA’s activities highly and increased its budget over the period 2005–2010 to accelerate progress. Another example is the Institute for Pure and Applied Mathematics (IPAM) established at University of California, Los Angeles (UCLA). The IPAM was founded in 2000, just after the publication of the Odom Report. Its mandate is to foster the interaction of mathematics with all of science and technology, to build new interdisciplinary research communities, to promote mathematical innovation, and to engage and transform the world through mathematics. It offers two or three 3-month-long programs every year as well as shorter programs such as 1-week workshops. Both the IMA and IPAM are among eight NSF Mathematical Sciences Research Institutes (<http://www.mathinstitutes.org/>). As well as the Isaac Newton Institute, IMA, and IPAM, the Lorentz Center at Leiden University, the Netherlands, provides a good environment for international workshops at the forefront of the sciences including mathematics.

With respect to applied mathematics, in 2008 the US Department of Energy (DOE) published “*Applied Mathematics at the U.S. Department of Energy: Past, Present and View to the Future*”, which has come to be known simply as the *Brown Report*. In regard to energy policy, applied mathematics is more important. In particular, computational simulations of large-scale complex systems, such as regional and global climate, fluid dynamics of water, and electromagnetic fields of plasma (for nuclear fusion), are the main targets. Risk analysis is also significant. They argued that mathematics is important in improving models and overcoming the difficulties

solving problems, such as the uniqueness and reconstruction methods for inverse problems. The *Multiscale Mathematics Initiative* is another program that the US DOE promoted in 2000. Macroscopic phenomena and properties of matter arise from the microscopic processes of atoms and molecules. However, there are many hierarchical layers between the micro- and macro-scale, and so far, different theories and models used in computations have been developed to analyze the various phenomena that exist in each hierarchical layer. Multiscale mathematics aims to create a unified framework for the simulation of macroscopic phenomena by combining all physical and chemical processes from the microscale to the macroscale. The roadmap to create multiscale mathematics was compiled in 2004 and the program was carried out over 3 years, from 2004 to 2006. About 60 % of the budget was approved for topics from materials science and mathematical methodologies and tools applicable to, for example, the creation of nanomaterials. Micro/nano-fabrication techniques for integrated circuits were developed.

In 2008, the OECD published “*Report on Mathematics in Industry*.” In its introduction, the report clearly noted that industrial innovation is increasingly based on results and techniques of scientific research, and that much research is underpinned and driven by mathematics. They organized the *Global Science Forum (GSF)* and discussed mechanisms for strengthening the connection between mathematics and industry. They presented results of their assessment at the International Congress on Industrial and Applied Mathematics (ICIAM) conference (2007). They also discussed these problems with mathematicians and applied mathematicians. Through these attempts, the importance of the interaction between mathematics and industry is gradually making in-roads among policy makers, (applied) mathematicians, and industry people. Indeed, some big projects promoting the application of mathematics such as *Mathematics of Planet Earth 2013* and the Deutsche Forschungsgemeinschaft (DFG) Research Center Matheon, are progressing. Some books reporting on the present status of the mathematics–industry cooperation have been published [LER, GK].

In recent years, the importance of the use of “*Big Data*” is increasing year by year. Also, in materials science, it has been pointed out that it is crucial to rationalize the design and development of materials and tighten the development cycle by constructing databases of research results related to materials, and analyzing Big Data from Informatics Theory and Mathematics. In 2011, the US launched the “*Materials Genomics Initiative*” (MGI) to develop infrastructure to accelerate the discovery of advanced materials, especially through the use of computational capabilities, data management, and an integrated approach. Described in the following sections, a pioneering approach by the Advanced Institute for Materials Research (AIMR), Tohoku University, to building a mathematical foundation to predict structure and function of materials is quite timely in putting forth highly-functional numerical calculations for predictive capabilities of materials properties.

Another US program, “*Science at the triple point between mathematics, mechanics and materials science*,” started in 2011, is up and running. The project run by the Partnerships for International Research and Education (PIRE) is a 5-year NSF-funded international collaboration program that began in 2011. The main topics come

from applied mathematics and mechanics, including partial differential equations, calculus of variations, and scientific computation, which find use in materials science.

In Japan, a movement toward collaborations between mathematics and other fields was slightly delayed. This was noted in the report “*Mathematics as deserted science in Japanese S&T policy*,” published by the *Ministry of Education, Culture, Sports, Science and Technology (MEXT)*, Japan. In recent years, however, this movement quickly gained momentum through the establishment of the *JST CREST/PRESTO* program “*Alliance for Breakthrough between Mathematics and Sciences (ABMS)*” led by Yasumasa Nishiura. In this program, various research proposals related to materials science have been accepted and new fields for mathematics–materials science collaboration are beginning to open up. The accepted proposals include:

- CREST
  - A Mathematical Challenge to a New Phase of Material Science (Team Leader: Motoko Kotani)
- PRESTO
  - Resolution of Fine Structures of Block Copolymers by Young Measure and its Development (Yoshihito Oshita)
  - Global Analysis on Geometric Variational Problems and its Applications (Miyuki Koiso)
  - Development of New Dynamical Simulation Methods by Applying Mathematics (Naoshi Ichinomiya)
  - Mathematical Physics on Interfacial Tension in Nonequilibrium Systems (Hiroyuki Kitahata)

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