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Excerpt
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Introduction

1.1 Atoms

The virtually infinite variety of phenomena – the properties of matter, living and non-living, its behaviour and transformations – are manifestations of the various ways in which a limited number of structural units – *atoms* – can combine with each other to build up more intricate structures. This is now common knowledge. When it was proposed by Democritus and Epicurus in the fourth century BC, it was an astonishing hypothesis. A definitive exposition of the Democritean atomic hypothesis, *De Rerum Natura*, was written by Lucretius (*c*. 60 BC) (English translation by R. E. Latham: Lucretius (1994)). Through the medium of an epic Latin poem, Lucretius demonstrates how numerous familiar phenomena can be rationally accounted for on the assumption that 'there exists only atoms and empty space'. Its intuitive insights and uncanny premonitions of modern physics are all the more amazing in view of the fact that experimentation was of no great interest to editors of the Greek philosophers – the arguments are based on thoughtful observation of familiar things. The recent elucidation of the anti-Kythera mechanism, a mechanical device from the time of Lucretius like an orrery, for predicting the positions of celestial objects, which could perhaps be used for determining the longitude, shows that the experimental tradition of Archimedes continued.

Lucretius, in criticising the theory of Anaxagoras, even describes what we might now call 'fractals': 'in speaking of the *homoeomeria* of things Anaxagoras means that the bones are formed of minute miniature bones . . . gold consists of grains of gold . . . fires of fires . . .'

Concerning the number of elements, Lucretius wisely refused to enter into unfounded metaphysical speculations, saying only that the number of different kinds of atom is finite. The traditionally held view, opposed by Lucretius, was that there are just *four* elements: earth, fire, air and water, which were supposed to correspond symbolically to the four regular polyhedra, cube, tetrahedron, octahedron

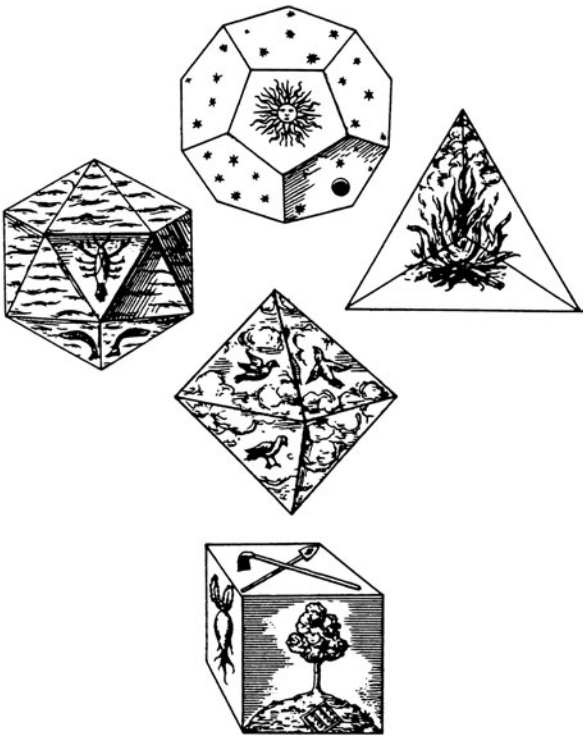

Figure 1.1 The five Platonic solids and the four elements; from Kepler's *Harmonice Mundi* (Kepler 1619).

and icosahedron (Figure 1.1). (The fifth regular polyhedron, the pentagonal dodecahedron, corresponded to the mysterious 'fifth essence' – the notion underlies the etymology of *quintessential*.)

In Plato's view, the correspondence between the four elements and four regular polyhedra was not only symbolic – he proposed that these polyhedra corresponded to the actual *shapes* of the atoms. For this reason the regular polyhedra are referred to as the 'Platonic solids'. Even the strangest ideas can contain a grain of truth: the regular and the semi-regular polyhedra ('the 5 Platonic and 13 Archimedean solids') are indeed prominent features in the microstructure of solids and liquids, but in the shapes of *clusters* of atoms rather than of individual atoms. Plato, in his 'Timaeus', sees the polyhedra as themselves built of 45-90-45 degree and 60-90-30 degree triangles, which are just the figures still to be found in a school geometry set. The five symmetrical 'Platonic' configurations were already known a millenium before the time of Plato. Over 400 carved stone balls from neolithic times have been found at various sites in northern Scotland. The Universities of Aberdeen and Glasgow possess extensive collections of these objects. A particularly fine set of five,

Figure 1.2 Scottish neolithic stone carvings corresponding to the regular polyhedra, in the Ashmolean Museum, Oxford. Their purpose is unknown. Photo by Graham Challifour for Critchlow (1979). Reproduced by kind permission of Graham Challifour and Keith Critchlow.

exhibiting the five configurations, is owned by the Ashmolean Museum, Oxford (see Figure 1.2).

The notion of the *four elements* had a powerful hold over scientific thinking until surprisingly recent times. Joseph Priestley discovered the element oxygen in 1774. Antoine Lavoisier repeated Priestley's experiments and understood their significance: air is composed of several gases, and oxygen is one of them. He also suggested that water, too, is a compound. These insights marked the beginnings of modern chemistry. This was the response of Antoine Baumé (1728–1804), the speaker of the Paris Academy of Science: 'The elements or base components of bodies have been recognised and determined by physicists of every century and every nation. It is inadmissible that the elements recognised for 2000 years should now be included in the category of compound substances. They have served as the basis of discoveries and theories . . . We should deprive these discoveries of all credibility if fire, water, air and earth were no longer to count as elements.'

This epitomises the fact that human beings, like crystals, are creatures of habit. Ways of approaching problems, once they have proved successful, tend to become rigidified into traditions. The history of science is replete with examples of how well-established patterns of thought have hampered the emergence of new developments that, once they have emerged, open up new worlds for exploration.

1.2 Geometry

For more than 2000 years mathematicians took it for granted that geometry, as systematised and presented by Euclid, was the only possible geometry, until the discovery by Bolyai and Lobachevski in the nineteenth century of 'non-Euclidean geometry'. The geometry of Bolyai and Lobachevski is the geometry of the hyperbolic plane, H_2, which readily generalises to *hyperbolic spaces*, H_n. The hypersurfaces S_n of hyperspheres in Euclidean spaces E_{n+1} give another family of non-Euclidean geometries. (The subscripts indicate the dimensions of the space in question). Spherical trigonometry – geometry on the surface of a sphere – is the geometry of S_2; it was investigated by Hipparchus (150 BC) and the basic theorems are in the *Spheraeca* of Menelaus and in Ptolemy's *Almagest*. Two thousand years passed before anyone noticed that this is a *non-Euclidean* geom-etry of two dimensions! The spaces E_n, S_n and H_n are spaces of constant Gaussian curvature (zero, positive and negative, respectively). The formulae of hyperbolic geometry H_2 are just those of the geometry on the surface of a sphere, but with the radius of the latter set to i, the square root of minus one. Riemann generalised still further, developing the geometry of spaces in which the metrical properties varied continuously from point to point – a generalisation to higher dimensions of the intrinsic metrical properties of surfaces, which had been investigated by Gauss. The most general – and in a sense the most primitive – kind of geometry is topology, which takes no account of metrical properties; it deals only with the continuity and combinatorial properties of geometrical figures.

Although material structures, of course, exist in three-dimensional (3D) Euclidean space, some of the more exotic geometrical concepts have recently entered into the materials sciences, providing new and stimulating ways of thinking about these structures. We shall occasionally touch upon some of these developments, which serve to indicate the increasingly important role of mathematics in the science of materials.

1.3 Crystallography

A major mathematical contribution to our present understanding of the atomic constitution of crystalline solids was the work of Schoenflies, Fedorov and Barlow which classified triply periodic patterns in E_3 – there are just 230 different possible types, characterised by their symmetries. The geometrical theory of the symmetries of all possible crystals is one of the triumphs of nineteenth century mathematics. It is an elaborate edifice built on the basis of a simple assumption, namely that an 'ideal' crystal consists of an infinite number of identical units arrayed in space so that all have identical surroundings.

The experimental verification came with the introduction of X-ray structure analysis. The diffraction of X-rays by crystals was discovered by Max von Laue in 1912. He received a Nobel prize for this discovery two years later. Lawrence Bragg, the developer of the method along with his father William Bragg, revealed the atomic structure of sodium chloride as an array of alternating sodium and chlorine ions like a three-dimensional chessboard. Lawrence Bragg heard the news of his Nobel prize in 1916 while serving as an officer on the Western Front. With their technique they were able, by 1923, to laboriously produce pictures of the atoms of calcium, silicon and oxygen arranged in the mineral diopside. Since then, the arrangement of atoms in all matter, living and non-living, has been the basis of our understanding of its properties and behaviour.

Along with the development of X-ray diffraction techniques, the 230 space groups became the key to understanding crystalline structures. A picture emerged of a 'perfect' solid consisting of an arrangement of atoms 'decorating' the interior of a unit cell, which, repeated by translation, produces the whole structure. Unfortunately, this elegant scheme for a long time had a constraining effect on crystallographers somewhat analogous to the effect of Euclid's scheme on geometers. It became the paradigm. Important features of real materials were called 'defects' and materials that did not fit the scheme were dismissed as 'disordered'.

1.4 Generalised Crystallography

The discovery of quasicrystals has brought home forcefully to crystallographers the fact that a material structure could be highly ordered without being periodic. There are other, perhaps more interesting, ways in which structures can be orderly and systematic. Atoms and molecules know nothing of unit cells and they know no group theory; they simply respond to their immediate collective environment. Triple periodicity, when it arises, is a necessary consequence – an epiphenomenon – of more localised ordering principles. (An amusing illustration of the dominance of old ways of thinking is the modelling of quasicrystal structure in terms of a *pair* of 'unit cells' instead of one!)

A detailed understanding of how large-scale order (of any kind, not necessarily periodicity) arises from local ordering principles remains elusive. A theorem, due to Boris Nikolaievich Delone (Delone *et al.* 1934; 1976) throws some light on the way in which periodicity can arise from purely local conditions. A *Delone set* (r, R) in E_n is a set of points with the property that every sphere of radius r contains at most one of the points and every sphere of radius R contains at least one of the points (i.e. the points can be thought of as centres of hard spheres of radius r, and there are no large voids in the arrangement). Suppose, further, that for some length ρ, the configurations within spheres of radius $\rho + 2R$ centered at the points of the set are all congruent, and that the symmetry of this configuration is the same as the symmetry of the configuration within a radius ρ. Then *the point set is* (n-tuply) *periodic*. A simple proof of this assertion has been given by Senechal (1986). In E_2, ρ can be taken to be $4R$ and in E_3 it is conjectured that $\rho = 6R$.

The proposal that the scope of theoretical crystallography could, and should, be extended to embrace the study of systematic structures more general than the classical triply periodic structures of 'perfect' crystals, has long been advocated

(Bernal & Carlisle 1968; Mackay 1975). For a major portion of the twentieth century experimental crystallography was dominated by X-ray diffraction – a circumstance that restricted theoretical crystallography mainly to those structures that could be understood and described in terms of lattices and their reciprocal lattices. X-ray diffraction detected and emphasised the periodicities of a structure. In recent decades new experimental and observational techniques have become available, especially high-resolution electron microscopy, and have made 'generalised crystallography' a real possibility. Crystal structure analysis using the scattering of X-rays by crystals of the material under investigation has been such an enormously successful technique that other methods have been eclipsed. The technique has been to crystallise many copies of the molecule under investigation and effectively to use this ordered array as an amplifier of the scattering from a single molecule. To see atoms individually in less regular structures required the development of electron microscopy which has only recently reached the necessary resolving power. With this and other techniques, such as atomic force microscopy, the elaborate ordering of the atoms in both living and inorganic materials has begun to be revealed. In real materials we usually find several levels of organisation with different rules at each level. *Hierarchy* is the characteristic, in particular, of living systems. The present period has seen a rising appreciation of the ways in which structure and information are intimately connected. This was epitomised in the most important discovery of the twentieth century, the double helix of DNA, where the material structure encodes information as a sequence of base pairs. The general principle underlying this encoding of genetic information in an 'aperiodic crystal' had already been foreseen by Erwin Schrödinger in his book *What is Life*? (Schrödinger 1944). At the same time, immense computational power has developed, enabling the geometry of very complex structures to be handled and to be presented as computer graphics.

1.5 Shapes and Structures

The English and Scottish traditions of science, far more than the Continental, have been based on model-making, on *visualisation* and on analogy with everyday mechanisms rather than on words, formulae and logic-chopping. J. C. Maxwell, William Thomson (Lord Kelvin), W. H. D'Arcy Thompson, W. L. Bragg and J. D. Bernal are some of the masters of this British tradition, while Descartes, Gödel, Euler, Heisenberg, Claude Bernard, epitomise the Continental Schools, the attitude of which was exemplified by Pierre Duhem (1861–1916).

In 1917, in the middle of World War I, D'Arcy Wentworth Thomson in the University of Dundee produced his magnum opus *On Growth and Form*, in which he applied simple mathematics and physics to the problems of the multifarious shapes encountered in the living world.

It is clear that, even though considerable knowledge was available at the time, D'Arcy Thompson (1860–1948), did not wish to take atoms and microstructure at the atomic level into account. He mentioned the atomicity of matter only once or twice and even in the second edition (1942) took little note of the atomic level. His work was concerned with illuminating the underlying mathematical principles governing the shapes of living organisms at a macroscopic scale, stopping short at the level of things visible with a simple microscope.

A transitional manifesto, *Structure in Nature is a Strategy for Design* by an architect, Peter Pearce (1978) has been influential, just before the computer period, in introducing the geometry of polyhedra and related regular three-dimensional structures to a wider world so that the dominance of cubic structures in our culture has been reduced. Robert Williams' *The Geometrical Foundations of Natural Structure* (1979) takes a similar approach, taking examples of intricate polyhedral structures from the geometry of complex arrangement of atoms in crystalline materials. We must mention too the vital role played by H. S. M. Coxeter in reviving a general interest in geometry and educating several generations throughout his long life and particularly with his textbook *An Introduction to Geometry* (1969). Grünbaum and Shephard wrote: 'mathematicians have long since regarded it as demeaning to work on problems related to elementary geometry in two or three dimensions, in spite of the fact that it is precisely this sort of mathematics which is of practical value.'

Our aim, then, in the chapters which follow, is to survey some of the important developments that have been taking place in recent decades in our understanding of the structure of complex materials, with the emphasis on the underlying geometrical principles.

Johannes Kepler (1571–1630) can be regarded, for many reasons, as the initiator of this approach. It was Kepler who produced for the first time a rigorous enumeration of the 'regular' tilings of the plane. He also considered tilings that include regular pentagonal tiles and so came close to the concept of aperiodic patterns more than 300 years before the Penrose tilings and the discovery of quasicrystals. He rediscovered the 13 semi-regular polyhedra and discovered the rhombic triacontahedron, which is now known to be an important key to the structure of icosahedral quasicrystals. It was Kepler who suggested that the hexagonal symmetry of snowflakes could arise from a close packing of identical subunits, and it was Kepler who guessed, correctly, that the densest possible packing of spheres is the arrangement now known as 'cubic close packing' (Kepler 1611). Robert Hooke, applying the microscope for the first time to everything within his reach, began to realise a science of the structure of matter. Figure 1.3 is taken from Hooke's *Micrographia* (Hooke 1665).

We close this chapter with a picture (Figure 1.4) of a portion of Kepler's configuration of nested regular polyhedra, which he believed could account for the radii of planetary orbits. His unusual mental flexibility allowed him to abandon it and go on to

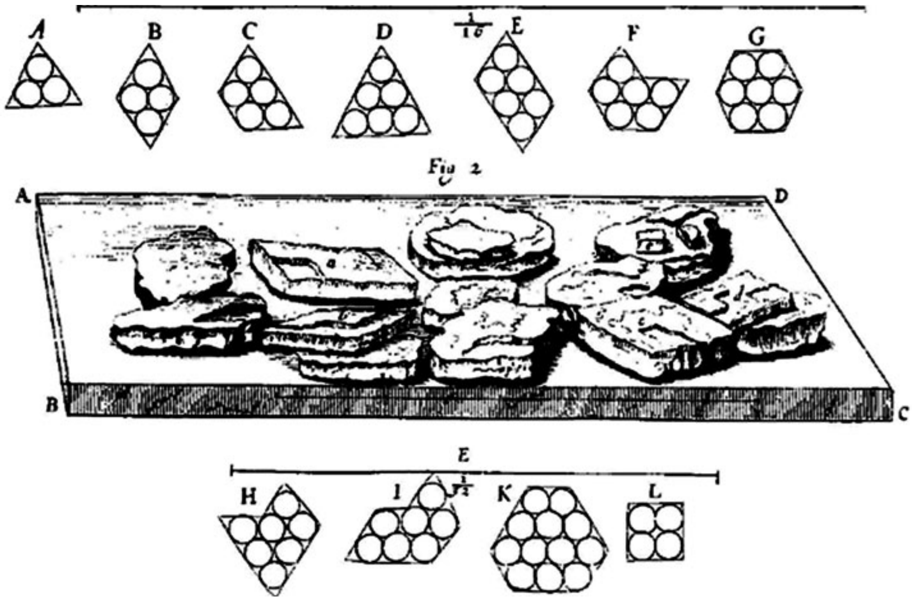

Figure 1.3 Crystalline structure from Robert Hooke's *Micrographia* (Hooke 1665).

discover the three famous fundamental laws of planetary motion. It may seem strange that we choose to pay tribute to Kepler's genius by thus drawing attention to a case where his remarkable intuition led him astray. However, the model epitomises the perennially fascinating attraction, for the human mind, of the five regular polyhedra. And the model now seems strangely prophetic – configurations of *nested regular and semi-regular polyhedra* have recently re-emerged in the striving of scientists to reveal Nature's structural principles, this time in a quite different context – as models of the clusters of atoms that occur in the building up of complex crystalline solids.

Figure 1.4 The portion of Kepler's configuration of nested regular polyhedra, representing the orbits of the inner planets. From Kepler's *Mysterium Cosmographicum* (1596).

2

2D Tilings

A *doubly periodic* pattern in the plane has a symmetry group containing two independent translations. Two translation vectors determine a parallelogram. A parallelogram whose sides have lengths and directions corresponding to two of the translations is a *primitive unit cell* of the pattern, provided there is no smaller parallelogram formed from translation vectors. Applying the translations to a single point generates a *lattice*. The whole pattern is produced by repeated application of the portion of the pattern within a primitive unit cell, by translating the cell. There are 17 discrete subgroups of the Euclidean group of the plane that contain two independent translations (see for instance Schattschneider (1978) for a simple introduction). They are the *wallpaper groups*, and patterns with these symmetry groups are ‘wallpaper patterns’. In the standard nomenclature for these groups the symbol p denotes the *primitive* unit cell, and c denotes a longer rectangular unit cell whose vertices *and centre* are vertices of primitive parallelograms. The p or c is then followed by a list of generators: 2, 3, 4 and 6 denote rotations through $2\pi/2$, $2\pi/3$, $2\pi/4$ and $2\pi/6$, m denotes a reflection and g denotes a glide (the combined effect of a reflection in a line and a translation along the direction of the line and equal to half a lattice translation).

A *tiling*, or *tessellation*, of a space is a subdivision of the space into non-overlapping regions (‘*tiles*’). The vertices and edges of a tiling constitute a *net*. Periodic nets in two or in three dimensions (2D or 3D) are of fundamental importance in the description of crystalline structure. In the simplest application vertices and edges corresponding to atoms and bonds, but highly complex structures can often be more readily understood and visualised by identifying an underlying net or framework in the structure – a topic we shall return to in a Chapter 8. O’Keeffe & Hyde (1980) have given an extensive and fascinating survey of 2D nets that occur in crystalline structures.

Doubly periodic patterns produced by tiling a plane have been exploited for their decorative possibilities by every civilisation, for thousands of years. The ingenuity of medieval Islamic craftsmen is particularly noteworthy, and often quite

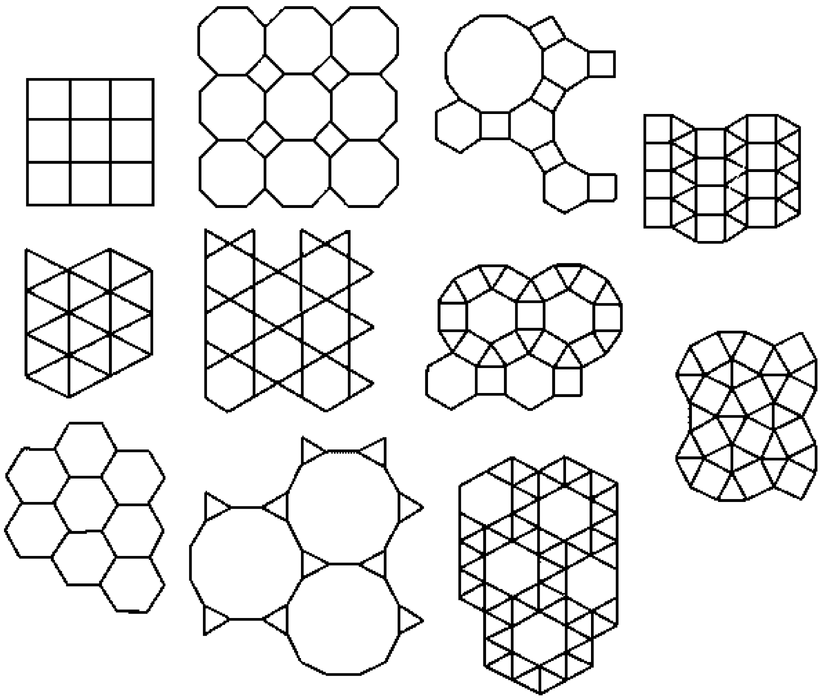

Figure 2.1 The eleven uninodal ways of tiling the plane with regular polygon tiles.

amazing (Bourgoin 1879; El-Said & Parman 1976; Critchlow & Nasr 1979; Chorbachi 1989).

2.1 Kepler's Tilings

The first known example of a mathematically rigorous approach to a tiling problem is probably Kepler's enumeration of all possible tilings of the plane by regular polygons, with the proviso that all vertices shall be identically surrounded (Kepler 1619).

Suppose that the generic vertex is surrounded by n_3 equilateral triangle, n_4 squares, and so on. The total angle around the vertex is 2π. This gives

$$\sum_{p=3}^{\infty} (p-2)n_p/p = 2$$

Eleven solutions lead to tilings of the whole plane. In an obvious notation, that lists the values of p encountered as the vertex is circumnavigated, we have:

3^6 4^4 6^3 $3^4.6$ $3^3.4^2$ $3^2.4.3.4$ $3.4.6.4$ $3.6.3.6$ 3.12^2 $4.6.12$ 4.8^2

Portions of these tiling patterns are illustrated in Figure 2.1. The tiling $3^4.6$ exists in two enantiomorphic versions. The tiling 3.6.3.6 is called the 'kagome' pattern