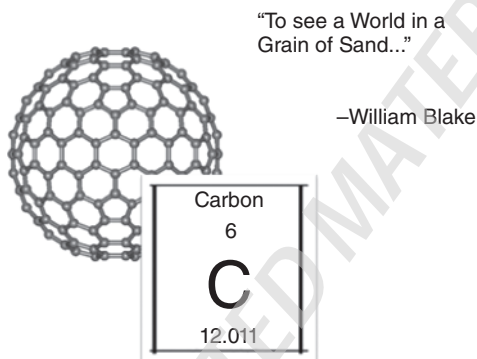


Introduction*



“Dimensionality” and “atomic ordering in finite structures” seem like rather odd principles by which to organize thoughts on solid-state physics. Indeed, this is not a historical approach to understanding solids at all. However, in learning *solid state* today, we must embrace the historical orthodoxy of crystal lattices, phonons, and band structure, as well as a whole *zoo* of emerging exotic materials that range from fullerenes to organic superconductors.

How do we understand two-dimensional (2D) dichalcogenides, atomically layered permanent magnets, perovskites, topological insulators, conducting polymers, quantum dots, graphene, glassy carbon, etc.? And what of the low-dimensional analogues of orthodox collective behavior: charge density waves, excitons, spin waves, and the like? We know these things “live” in/on such low-dimensional structures. An interesting and instructive way to build a framework is to begin with the normative behavior of a special atom, *carbon*, and the *dimensionality* of the structures it makes. Why carbon? Because among the elements it is about the most robust at making compounds and structures. It is extremely flexible in how it chooses to arrange itself. Why dimension? Well, lower-dimensional materials offer new approaches to technology, holding

*Historical Note: some of the hand-drawn images of the text have their origins in the very first edition of *One-Dimensional Metals*. They are an interesting and important reminder of what our state of mind was at a time when *dimensionality* was a new and mysterious science.

the key to everything from quantum computers to new medicines. But most importantly, it introduces the idea of “topology.”

Look, the traditional story goes like this. We begin our description of solids with an infinite mathematical construction (the lattice) given by specific point group symmetries. Onto the lattice points we attach some arbitrary set of atoms (generally picking something found in nature). We calculate specified properties based upon idealizations of how free the electron may be at each lattice point or how free the motion of the atom at the lattice point may be. We *adiabatically* add interactions between vibrations, carriers, etc. of the lattice to get more interesting phenomena.

Our story, though, is like a tale of *die Brüder Grimm*¹: carbon is the central atom of the universe.² It forms more compounds in more ways than any other atom. Thus, other atomic systems deviate from carbon by breaking its norms of symmetry. Beginning with large carbon molecules, we form nanometer structures. As we add, subtract, or substitute C atoms in the structure, we design materials with properties that can be examined through the dimensional change we have brought out. It isn't quite a chemical point of view, and it isn't quite solid-state physics in its purest form. It is the type of conversation you hear in working research labs across the world: complementary and an *enjoyable compromise* between the perspectives.

1.1 Dimensionality

The concept of *dimensionality* has been with us for a while, and it is an intellectually appealing concept. Speaking of a dimensionality other than three will surely attract some attention. Some years ago it was fashionable to admire physicists who apparently could “think in four dimensions” in striking contrast to Marcuse's *One-Dimensional Man* (Figure 1.1) [1]. Physicists would then respond with the understatement: “We only think in two dimensions, one of which is always time. The other dimension is the quantity we are interested in, which changes with time. After all, we have to publish our results as two-dimensional figures in journals. Why should we think of something we cannot publish?”

This fictitious dialogue implies more than just sophisticated plays on words. If physics is what physicists do, then in most parts of physics there is a profound difference between the dimension of time and other dimensions, and there is a logical basis for this difference [2]. In general, the quantity that changes with time and in which the physicist is interested is some *intrinsic* property of an object.

1 The Brothers Grimm wrote fairy tales in the southern part of Germany around the early 1800s. In 1812 they published their first collection of folk tales, *Kinder- und Hausmärchen* (Children's and Household Tales). Their hometown was only a short drive from the author's laboratory at the borders of the Black Forest (where many of their tales were set). They are responsible for almost as many nightmares as organic superconductors!

2 This is clearly a biased and self-indulgent statement, and should only be taken metaphorically. Si-based life forms would certainly have a different opinion. Note that when we say “Si-life” we do not distinguish between that life based on a processor and life based on Si-regulated metabolic mechanisms.



Figure 1.1 Marcuse's man. Simultaneously with Herbert Marcuse's book *One-Dimensional Man*, which widely influenced the youth movement of the 1960s. W.A. Little's paper on "Possibility of Synthesizing an Organic Superconductor" was published, motivating many physicists and chemists to investigate low-dimensional solids.

The object in question is typically imbedded in a three-dimensional (3D) space. Objects themselves, however, may be very flat such as flounders, saucers, or oil films with greater length and width than thickness. In materials such as graphene or MoS_2 , thickness can be negligibly small – atomic. Such objects can be regarded as (approximately) 2D. Now, if the intrinsic property that the physicist wishes to study is somehow constrained in behavior, in direct correlation to the dimension of the object, like a boat on the 2D surface of the sea is hopefully constrained to 2D motion, then we say the property is *expressing the dimensionality* of the object. In our everyday experience one-dimensional (1D) and 2D objects and 1D and 2D constraints are more common than you might think. Indeed, low dimensionality should not be particularly spectacular to our expectations. For this reason too, it is reasonable to introduce non-integer, or *fractal*, dimensions [3]. Not much imagination is necessary to assign a dimensionality between one and two to a network of roads and streets – more than a highway and less than a plane. It is a well-known peculiarity that, for example, the coastline of Scotland has the *fractal dimension* of 1.33 and the stars in the universe that of 1.23.

Solid-state physics treats solids both as objects and as the space in which objects of physics exist, e.g. various silicon single crystals can be compared with each other, or they can be considered as the space in which electrons or phonons

move. The layers of a crystal, like the *ab*-planes of graphite, can be regarded as 2D objects with interactions between them that extend into the third dimension. But these planes are also the 2D space in which electrons move rather freely. Similar considerations apply to the (quasi) 1D hydrocarbon chains of conducting polymers.

1.2 Approaching Dimensionality from Outside and from Inside

There are two approaches to low-dimensional or *quasi*-low-dimensional systems in solid-state physics: geometrical shaping as an *external approach* and increase of anisotropy as an *internal approach*. These are also sometimes termed *top-down* and *bottom-up* approaches, respectively. For the external approach, let us take a wire and draw it until it gets sufficiently thin to be 1D (Figure 1.2). How thin

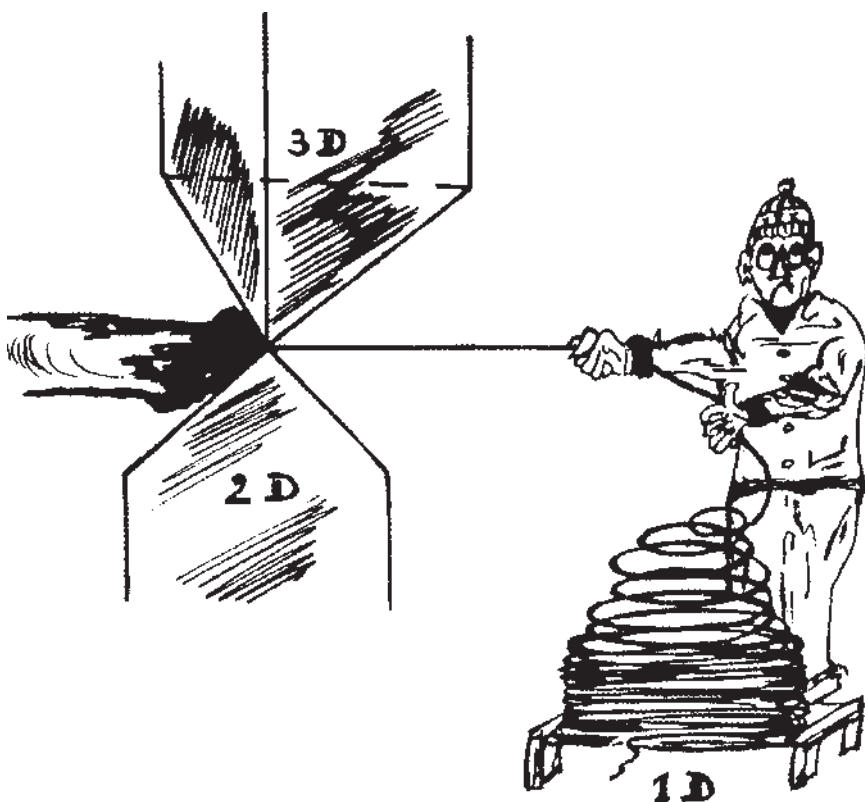


Figure 1.2 Wire puller. An “external approach” to one-dimensionality. A man tries to draw a wire through a mandrel until it is thin enough to be regarded as one-dimensional. Metallic wires can be made as thin as $1\ \mu\text{m}$ in diameter like this, but this is still far away from being one-dimensional. Lithographic processes using focused ion beams and focused electrons can produce some metal and semiconductor structures that are narrow enough to exhibit one-dimensional properties (\sim nanometers).

will it have to be to be truly 1D? This depends a little on exactly what property of the structure is desired to express low-dimensional behavior. Certainly, thin compared to some microscopic parameter associated with that property. For example, for 1D electrical transport properties, the structure must have length scales such that the mean free path of an electron or the Fermi wavelength is affected by the physical confinement of the structure. We will discuss these concepts further a little later on in the text. But surely the meaning is clear: some fundamental aspect of an internal object responsible for the phenomenon of interest must be dramatically altered by its localization within the structure.

Technology today has made it possible to approach such sizes using methods of *lithography* as well as *chemical assembly*. Lithography is the top-down approach to creating confining structures as it whittles away material until only very small structures remain. Chemical assembly is the “bottom-up” approach, and it forms the structure through chemical reactions. The two approaches offer very different properties to the nanoscale structure created, both in terms of atomic ordering and control over object placement.

To achieve “one-dimensionality” does the wire puller in Figure 1.2 have to draw the wire so extensively that it is finally to become a monatomic chain? Well, the *Fermi wavelength*, a fundamental property of the carrier electron responsible for conductivity, becomes relevant when discussing the eigenstates of all the electrons of the structure. If electrons are confined in a box, quantum mechanics tells us that the electrons can have only discrete values of kinetic energy. The energetic spacing of the eigenvalues depends on the dimensions of the box – the smaller the box the larger the spacing (Figure 1.3):

$$\Delta E_L = h^2 / 2m(\pi/L)^2 \quad (1.1)$$

where ΔE_L is the spacing, L is the length of the box, m is the mass of the electrons, and h is Planck’s constant. For a box containing multiple electrons, the *Fermi level* is the highest occupied energy state (at absolute zero). The wavelength of the electrons at the Fermi level is called the *Fermi wavelength*. At finite temperatures, if the energy difference between levels is much larger than the thermal energy ($\Delta E_L \gg kT$), there are only completely occupied and completely empty levels (not accounting for spin). A thin wire is a small box for electronic motion perpendicular to the wire axis, but it is a very large box for motions along the wire. Hence, in two dimensions (radially), it represents an insulator, and in one dimension (axially), it is a metal! This is simply because the $\Delta E_{\text{radially}} \gg kT$ whereas $\Delta E_{\text{lengthwise}} \ll kT$.

If there are only very few electrons in the box, the Fermi energy is small and the Fermi wavelength fairly large. For *real* materials, these are the electrons that can participate in bonding–antibonding orbitals. This is the case for semiconductors at very low doping concentrations. Wires of such semiconductors are already 1D if their diameter is on the order of hundreds of Ångströms.

Such thin wires can be fabricated from silicon or from gallium arsenide by lithographic techniques, and effects typical for 1D electronic systems have been observed experimentally [4]. Systems with high electron concentrations have to be considerably thinner if they are to be 1D. It turns out that for a concentration of one conducting electron per atom, we really need a monatomic chain!

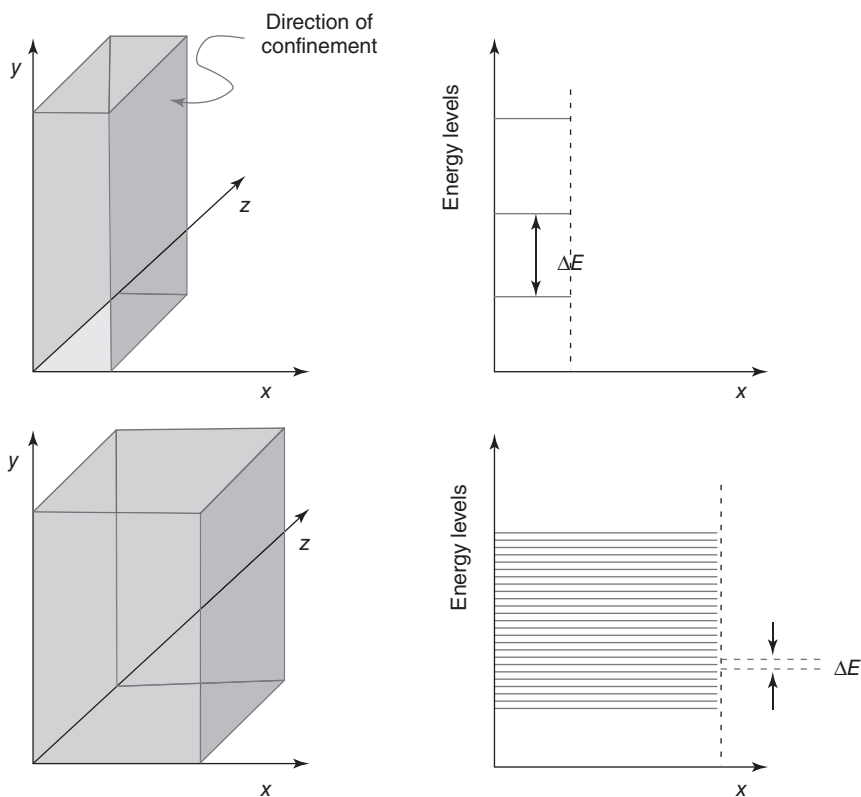


Figure 1.3 Electrons in small and large boxes and energy spacing of the eigenstates. This is an example of dimension based on confinement.

Experiments on single monatomic chains are very difficult to perform, so a bundle of chains is usually used. An example of such a bundle is polyacetylene fiber, consisting of some thousands of polymer chains, closely packed with a typical interchain distance of 3–4 Å. Certainly there are *some* interactions between the chains; however, in the case of small *interchain coupling*, it can be assumed that the net sum of the individual chains determines the properties of the bundle (Figure 1.4). The experiment becomes one of an *ensemble* of 1D chains.

Another method of geometrical shaping employs surfaces or interfaces (Figure 1.5). The surface of a silicon single crystal is an excellent 2D system, and there are various ways of confining charge carriers to a layer near the surface. Actually, the physics of 2D electron gases are an important part of today's semiconductor physics [5], and most of the 2D electron systems are confinements to surfaces or interfaces. The most fashionable effect in a 2D electron gas is the quantized Hall effect or von Klitzing effect [6]. A 1D surface, i.e. the edge of the crystal, is much more difficult to prepare and hardly of any practical use. But one can argue that exposing a sample to a magnetic field would be an excellent example of a 1D electronic system since electrons can be forced into motion along specific paths defined by the crystal and the field. In fact,

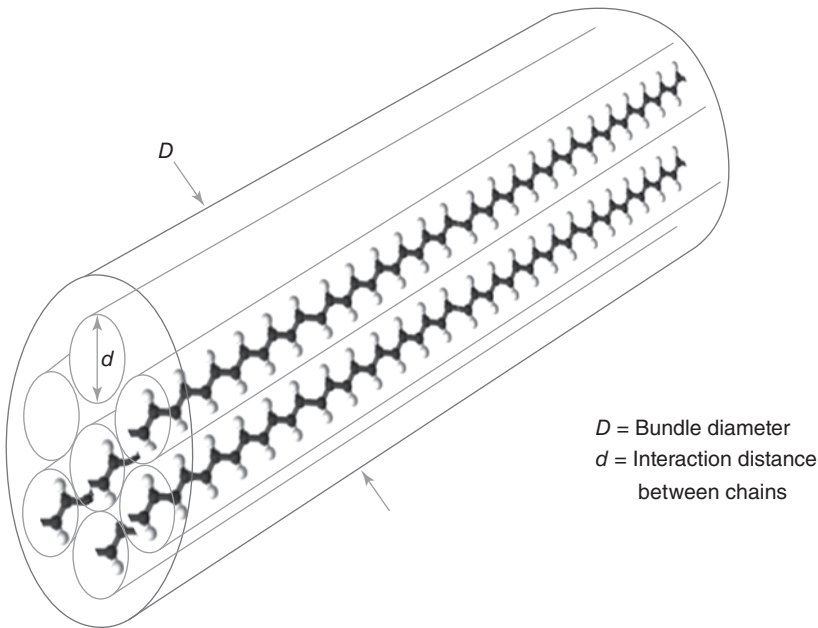


Figure 1.4 Experiments on individual chains are difficult to perform. But bundles of chains are quite common, for example, fibers of polyacetylene.

reducing von Klitzing's sample to "edge channels" is one way of explaining the von Klitzing effect [7].

The *internal approach* to 1D solids comprises the gradual increase of anisotropy. In crystalline solids the electrical conductivity is usually different in different crystallographic directions. If the anisotropy of the conductivity is increased in such a way that the conductivity becomes very large in one direction and almost zero in the two perpendicular directions, a nearly 1D conductor will result. Of course, there is no simple physical way to increase the anisotropy. However, it is possible to look for sufficient anisotropy in already existing solids that could be regarded as (quasi) 1D. Some anisotropic solids are compiled in the next chapter of this book. How large should the anisotropy be to meet one-dimensionality? A possible answer is: "Large enough to lead to an open *Fermi surface*."

The *Fermi surface* is a surface of constant energy in *reciprocal space* or momentum space. While the Fermi surface and reciprocal space will be discussed in detail later, for the discussion here, it is sufficient to imagine this surface as describing all of the electron states within the solid that are available to take part in electrical transport. For an isotropic solid, the Fermi surface is spherical, meaning that electrons can move in any direction of the solid equally well.

If the electrical conductivity is large in one crystallographic direction and small in the other two, the Fermi surface becomes disklike. The kinetic energy of the electrons can then be written as $E = p^2/2m^*$, resembling the kinetic energy of a free particle (p = momentum, m = mass), with the exception that the mass

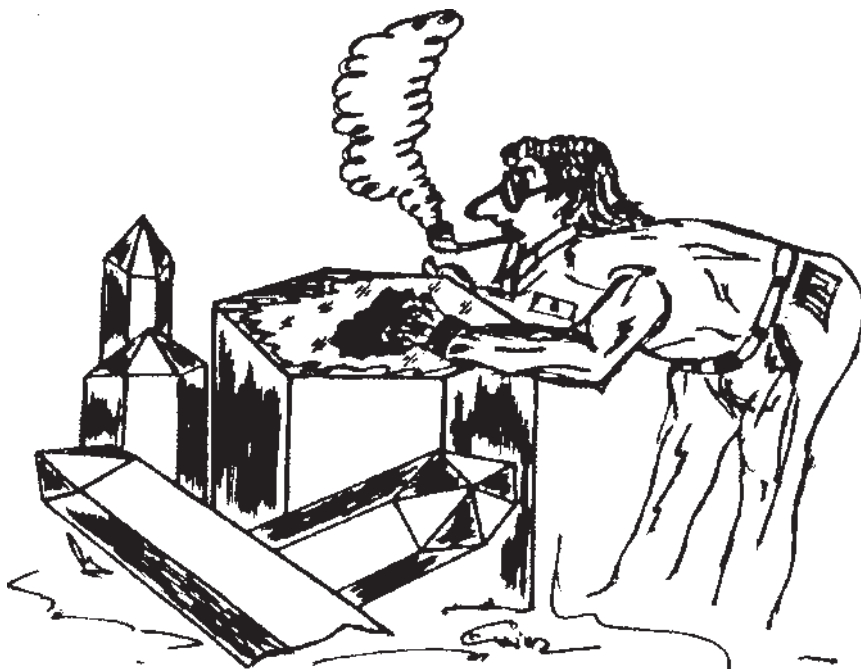


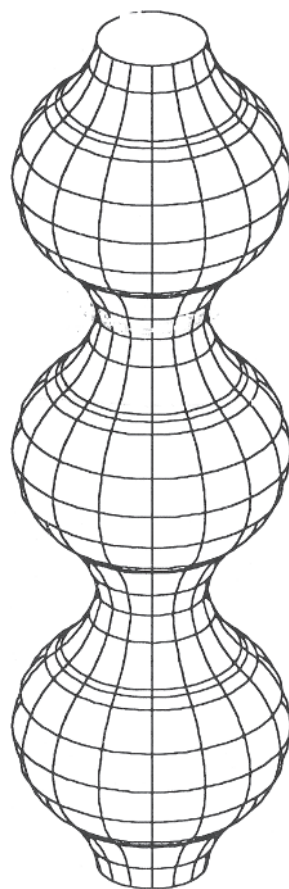
Figure 1.5 The crystal cutter. Crystal surfaces are excellent two-dimensional (2D) systems. The cutter here tries to improve the crystal face by mechanical polishing, but the qualities achieved by this method are not sufficient for surface science. Surface scientists cleave their samples under ultrahigh vacuum conditions and use freshly cleaved surfaces for their experiments – leaving large 2D planes of atoms. Another approach is to use highly oriented and polished crystals that are then sputtered with high current ion beams and annealed at high temperatures to reform the surface.

has been replaced by the *effective mass* m^* . The *effective mass* indicates the ease with which an electron can be moved by the electric field. If the electrons are easy to move, the conductivity is high. Easy motion is described by a small effective mass (small inertia), and p must also be small to keep E constant. If it is infinitely difficult to move an electron in a specific direction, its effective mass will become infinitely large in this direction, and the Fermi surface will be infinitely far away. However, the extension of the Fermi surface is restricted: if the Fermi surface becomes too large in any direction, it will merge with the Fermi surface generated by the neighboring chain or plane (“next Brillouin zone” in proper solid-state physics terminology) assuming this hypothetical solid is made up of stacked structures of some sort. This merging “opens” the Fermi surface, similar to a soap bubble linking with another bubble (Figure 1.6).

1.3 Dimensionality of Carbon: Solids

As promised, we now want to put these structures in the context of carbon. But again, why carbon? How will it be different from other atoms? Let’s contrast

Figure 1.6 Open Fermi surfaces, analogous to merged soap bubbles, as a criterion of low dimensionality. The Fermi surface belongs to a solid that is essentially two-dimensional. The solid will have no electronic states contributing to electrical conductivity along the axial direction but will easily conduct radially, normal to the axis.



it for a moment with a similar element silicon – the basis for much of today's technology. Silicon is unique among solids [8]: it is the most perfect solid producible. That is, there are fewer imperfections in a silicon single crystal than there are gas atoms in ultrahigh vacuum (per unit volume). It is the solid we know most about, and it is the solid that has largely influenced the vocabulary of solid-state physics. Carbon is located directly above silicon in the periodic table of the elements, and just as silicon is outstanding among the solids, carbon is outstanding among the elements. Carbon forms the majority of the known chemical compounds. Much of organic chemistry simply involves arranging carbon atoms (with hydrogen not having any specific properties but just fulfilling the task of saturating dangling bonds). In our context, carbon has the remarkable property of forming 3D, 2D, 1D, and zero-dimensional (0D) solids. This is related to the fact that carbon is able to form single, double, and triple bonds. This ability of carbon to form many types of bonds, at many different bonding angles, sets it aside from silicon in another important way; it leads to biology rather than technology.

1.3.1 Three-Dimensional Carbon: Diamond

Beginning with an example from silicon, diamond appears as the trivial solid form of carbon (Figure 1.7). Diamond has similar semiconducting properties to silicon. Both substances share the same type of crystal lattice. The lattice parameters are different ($a = 5.43 \text{ \AA}$ in silicon and 3.56 \AA in diamond), and the energy gap between valence and conduction band is larger in diamond, 5.4 eV , compared with 1.17 eV in silicon. Diamond is more difficult to manufacture and more difficult to purify than silicon, but it has better thermal conductivity and can be used at high temperatures. Since the costs for raw material change the final price of electronic equipment only slightly, some people believe that diamond is the semiconductor of the future. Silicon is typically used with added dopants to modify its electronic behavior. Doping diamond has proven to be far more difficult however. Here we mean doping to be a substitution of a lattice atom: in Si it would be Si, and in diamond it would be the substitution of a C, with another atom of different valency. The substituted atom adds carriers to the materials, changing its electrical properties. However, the potential dopant atom must fit into the lattice in some way, and this process must be better understood in diamond before the realization of high-quality diamond electronics.

Sometimes, semiconductors and metals are mentioned interchangeably in this book although they are quite different. The reason stems from the idea that a doped semiconductor can be regarded as a metal with low electron concentration. Here, “metal” is essentially used as a synonym for “electrically conductive, solid-state system.”

1.3.2 Two-Dimensional Carbon: Graphite and Graphene

In diamond the carbon atoms are tetravalent, that is, each atom is bound to four neighboring atoms by covalent single bonds. Another well-known naturally occurring carbon modification is graphite (Figure 1.8). Here all atoms are trivalent, which means that in a hypothetical first step only, three valence electrons participate in bond formation and the fourth valence electron is left over. The trivalent atoms form the planar honeycomb lattice, and the residual electrons

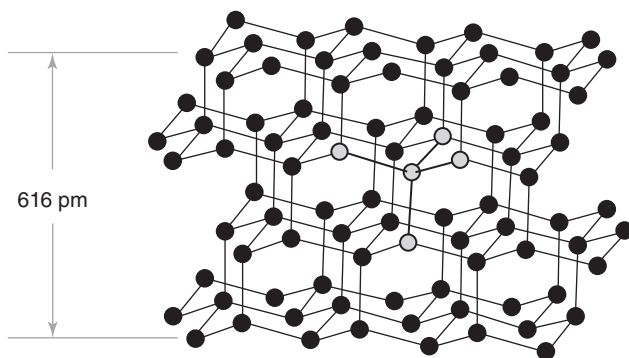
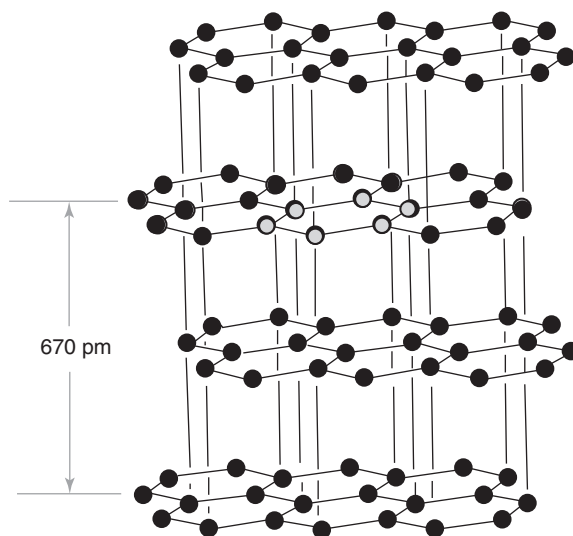


Figure 1.7 The diamond lattice. The diamond lattice can be seen as a “wavy” set of carbon planes connected together by carbon–carbon bonds.

Figure 1.8 The graphite lattice. A layered structure with very little interlayer interactions; graphite can have high in-plane conductivity of carriers and heat.



are shared by all atoms in the plane similarly to the sharing of the conduction electrons by all atoms of a simple metal (e.g. sodium or potassium). The various graphite layers only interact by weak van der Waals forces. In a first approximation graphite is an ensemble of nearly independent metallic sheets. In pure graphite they are about 3.35 \AA apart but can be separated further by intercalating various molecules. Charge transfer between the intercalated molecules and the graphitic layers is also possible. Graphite with intercalated SbF_5 shows an anisotropy of about 10^6 in electrical conductivity, conducting a million times better within a layer than between layers.

Diamond is a semiconductor and graphite is a metal (or semimetal). In diamond there are very few mobile electrons; in an undoped perfect diamond single crystal at absolute zero, there are exactly zero mobile electrons; and in graphite there are many, one electron per carbon atom. This difference is not due to dimensionality (three in diamond and two in graphite) but to single and double bonds. Several attempts have been made to build 3D graphite [9]. Theoretically it seems possible [10], but practically it has not yet been achieved.

Of course, since the layers of graphite are very weakly bound together, it is rather easy to separate them mechanically to form graphene – a single sheet of the honeycomb lattice. This lattice is truly 2D, since there is nowhere else for the electrons to go except upon the sheet that essentially defines their “world” for them. Notice though that this 2D sheet “samples” the 3D world in which it lives. If one takes the sheet and bends it in the third dimension while applying a field across it, one can induce phase accumulation in the wavefunction of its electrons – Berry’s phase, which comes from the geometrical intersection of the 2D and 3D worlds. Graphene has been studied extensively over the last few years, and transport in graphene led to the 2010 Nobel Prize in Physics [11]. By numbers, the density of graphene is 0.77 mg/m^2 . Its breaking strength is 42 N/m , the electrical conductivity is $0.96 \times 10^6 \Omega^{-1} \text{ cm}^{-1}$, and thermal conductivity is 10 times greater than copper. We will return to graphene in later chapters.

1.3.3 One-Dimensional Carbon: Cumulene, Polycarbyne, and Polyene

Carbon has an amazing ability to bond to itself in multiple ways. So “1D carbon” comes in several varieties. Using double bonds one can image a monatomic chain as Figure 1.9. (There are no dangling bonds in cumulene and in polycarbyne.) This substance is called *cumulene*; the name refers to the cumulative (meaning consecutive) double bonds. Any organic chemist will tell you that double carbon bonds can be *isolated* (separated by single bonds), *conjugated* (in strict alternation with single bonds), or *cumulated* (placed adjacent to each other) for a wide variety of compounds.

Cumulene has been synthesized for chains 5–10 carbons long [12]. While such long molecules are interesting, they fall a little short of a 1D wire, and polymeric cumulene has not been synthesized. Indeed, quantum chemistry predicts *polycarbyne*, an isomeric structure in which triple bonds alternate with single bonds, is preferred over cumulene. Polycarbyne is shown in Figure 1.10, and it is of particular interest to space scientists since it occurs in interstellar dust, meteorites, and in supernova remnants. It also is seen in trace amounts within natural graphite [13].

If we accept the simplification that in carbon compounds, hydrogen atoms just have the purpose of saturating dangling bonds (making them non-active) and that otherwise they do not contribute to the physical properties of the material, cumulene and polycarbyne are not the only 1D carbon solids. From this point of view, all polymers based on chain-like molecules are 1D.

Let’s learn some organic chemistry. On naming conventions, the ending “-yne,” as in polycarbyne, is used to indicate triple bonds. The ending “-ene” stands for double bonds and “-ane” for single bonds. A polyane is shown in Figure 1.11. (To add a little confusion to the subject, this substance is typically called polyethylene, ending with “-ene” instead of “-ane.” The reason is simply that the names of polymers are often derived from the monomeric starting material, which in this



Figure 1.9 One-dimensional carbon example one: cumulene.



Figure 1.10 One-dimensional carbon example two: polycarbyne.

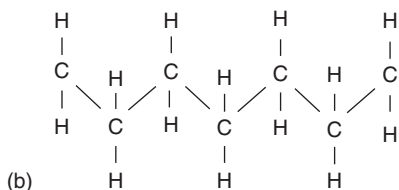
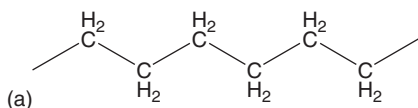


Figure 1.11 Polyethylene, as we might imagine the (a) polymerization of ethylene and (b) arrangement of bonding.

Figure 1.12 Polyacetylene, the prototype polyene, the simplest polymer with conjugated double bonds.

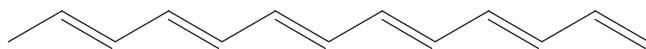
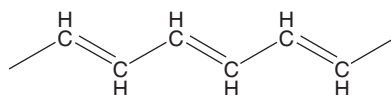


Figure 1.13 Polyacetylene using a simplified notation.

case is ethylene, $\text{H}_2\text{C}=\text{CH}_2$. Here the monomer contains a double bond, but during polymerization the double bond breaks to link the neighboring molecules.) Polyenes are insulators and of less interest in the context of this book. (Insulators are large bandgap semiconductors. Because of the large bandgap, it is difficult to lift electrons into the conduction band, and therefore the number of mobile electrons is negligible.)

Figure 1.12 shows polyacetylene, the prototype polyene, the simplest polymer with conjugated double bonds. The structure shown in Figure 1.12 is often simplified to the one in Figure 1.13, since by convention carbon atoms do not have to be drawn explicitly at the ends of the bonds and protons are neglected.

1.3.4 Zero-Dimensional Carbon: Fullerene

If we work our way down in dimensionality from *volume-diamond* to *plane-graphite* and *graphene* to *lines-polymers*, we will finally end up at the *point* as a 0D object. Do 0D solids exist outside of the obvious (the atom)? In semiconductor physics the “quantum dot” is well known [14]. Historically, this is a small disk cut out of a 2D electron gas. It is small compared to the Fermi wavelength, so that the electrons are restricted in all three dimensions of space (the 1D analogue to a quantum dot is often called “quantum wire”). Following the discussion in Section 1.2, a quantum dot is a 0D object. The present state of the art is to fabricate quantum dots containing more than 1 but less than 10 electrons. Because of the low electron concentration in semiconductors, such quantum dots can exhibit quite large diameters, up to several hundred Ångströms. More recently, quantum dots have been fabricated as chemically assembled nanoparticles, wherein the structure defines the confinement. Metal nanoparticles of Au, Ag, Cu, etc. have been created using a variety of chemical synthesis routes, and confinement of the electrons occurs at particle diameters of only a few nanometers. Likewise, quantum dots made from semiconductor materials such as Si, Ge, and compounds such as CdS, CdSe, PdS, etc. have been created. Following the rules we have already discussed, these nanoparticles can be many nanometers in diameter and still exhibit confinement because there are fewer electrons in the “box.” The ΔE between these electron states can be quite large, leading to some fascinating optical properties that are quite different from their bulk counterparts.

Carbon can form quantum dots in a number of ways – nanodiamonds, nanoplatelets of graphene, and others – as would be expected from carbon’s ability to bond in different ways. However, the most famous of these quantum dots of carbon in solid-state physics are the fullerenes [15]. The 1996 Nobel Prize

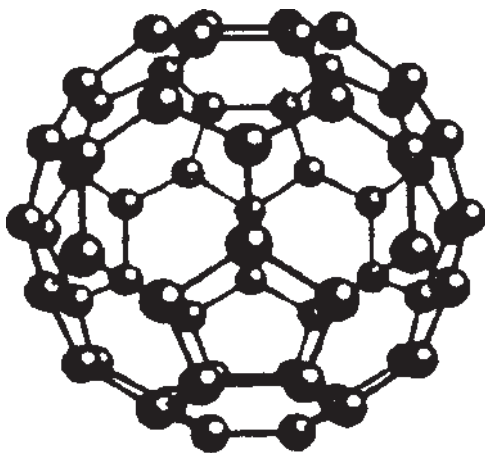


Figure 1.14 A fullerene molecule. This is an example of a C_{60} , but much larger cages can be made.

in Chemistry was given to R.F. Curl, H.J. Kroto, and R.E. Smalley for their role in the discovery of this class of molecules. Under certain conditions, carbon forms regular, cage-like clusters of 60, 70, 84, etc. atoms. A C_{60} cluster is composed of 20 hexagons and 12 pentagons and resembles a soccer ball (Figure 1.14), all bonded together as in graphene. The diameter of a C_{60} ball is about 10 \AA and thus is considerably smaller than that of a semiconductor quantum dot. However, in these carbon compounds, the electron concentration is higher than in inorganic semiconductors: in a system of conjugated double bonds, there is one π -electron per carbon atom! (More on π -electrons later.) In other words, there are 60 π -electrons in a fullerene ball of 10 \AA diameter, compared with some five electrons on a 100 \AA GaAs quantum dot. In quantum chemistry and solid-state physics, 60 is already a quite large number (we are used to counting: “one – two – many”). In fact, a 60-particle system is already a mini-solid, and a fullerene ball plays a dual role in solid-state physics: it is a mini-solid. It can also be a constituent of a macro-solid – fullerite.

We can study electronic excitations in the mini-solid and their mobility and interaction with lattice vibrations. At the same time it is possible to examine unexpected transport properties of the macro-solid, like superconductivity [16], photoconductivity, and electroluminescence [17]. Figure 1.14 shows the graphic representation of a fullerene mini-solid. Figure 1.15 schematically indicates the fullerene macro-solid.

1.4 Something in Between: Topology

Conceptually, we might conceive of a solid that is a combination of dimensions. Imagine, for instance, a single graphene sheet described in the section on graphite. Roll this conductive sheet into a seamless tube in which each atom is threefold coordinated as in the sheet. When the diameter of such a tube is between 14 and 200 \AA , we refer to the object as a *carbon nanotube*. For such an object, the electron wavefunction is confined to boxlike states around the

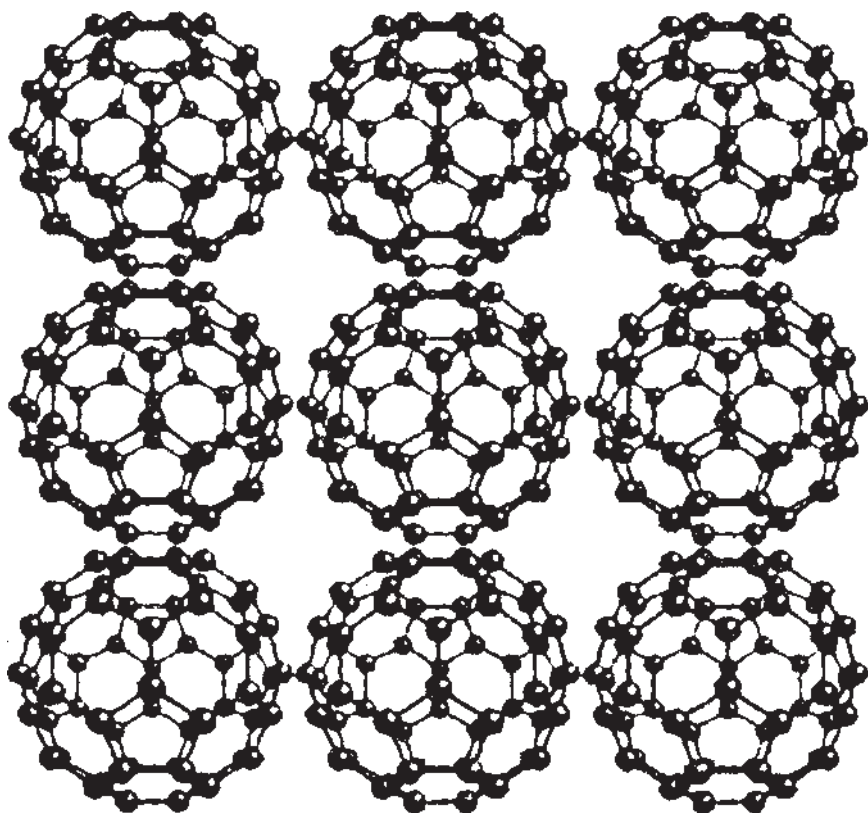


Figure 1.15 The fullerene crystal lattice: “fullerite.” These compounds have a rich chemistry. They can be doped by placing atoms between the balls, inside the balls, etc.

circumference. Along the axis of the tube, the electrons move in essentially a 1D system. Normally, this would appear to be similar to the semiconductor wires mentioned earlier. However, this circumference (or rolled-up) dimension allows for a set of spiral-like classical trajectories of the electron as it moves down the tube. In this way, if a 3D field (like a magnetic field) should penetrate the tube, the phase of the electronic wavefunction would be altered, resulting in Aharonov–Bohm effects. Thus, while the tube certainly has the character of a 1D system, it also has a “little more.” It is clearly not quite 2D however. For such systems, there is a *topology* that must be considered. That is to say, the object is connected together in such a way as to introduce an additional “dimensional” aspect. Here we mean a physical topology associated with a sheet of atoms rolled into the third dimension from a 2D starting point. However, the topological aspects of low-dimensional systems in general – or the way in which their electronic states might be connected together to form closed manifolds in space – will be a recurring theme. This is actually quite a natural outcome of the whole idea of working with low-dimensional materials. By restricting spatial dimension and confining the electronic wavefunction, we introduce boundary

conditions that are necessarily related to the overall connectedness of the object doing the confining.

1.5 More Peculiarities of Dimension: One Dimension

Aside from *topological effects*, when working with low-dimensional structures, what should we expect? Theory predicts that *strictly* 1D systems (for instance) will behave so unusually that the word “pathological” is often used. And if real systems appear less pathological than predicted, this is because real systems are only *quasi* and not strictly 1D. Real systems differ from ideal systems by having chains of finite rather than infinite length, sheets of finite area. In addition, the chains and sheets show imperfections such as kinks, bends, twists, or impurities. They are contained in an environment other than perfect vacuum, with neighboring structures at a finite distance and thus a nonzero interaction between them.

So, if you have ever followed a slow truck on a narrow mountain road, you have painfully experienced a very important aspect of one-dimensionality: obstacles cannot be circumvented! (Figure 1.16). A rather famous demonstration of 1D conduction studied by solid-state physicists is that of the monatomic metal wire. If one takes a very large number of gold atoms and places them very close to each other so as to form a wire, then the transmission of an electron down this wire is rather easily calculated. Now, we offer a very subtle change to this wire and replace in its center one gold atom for one silver atom and recalculate the

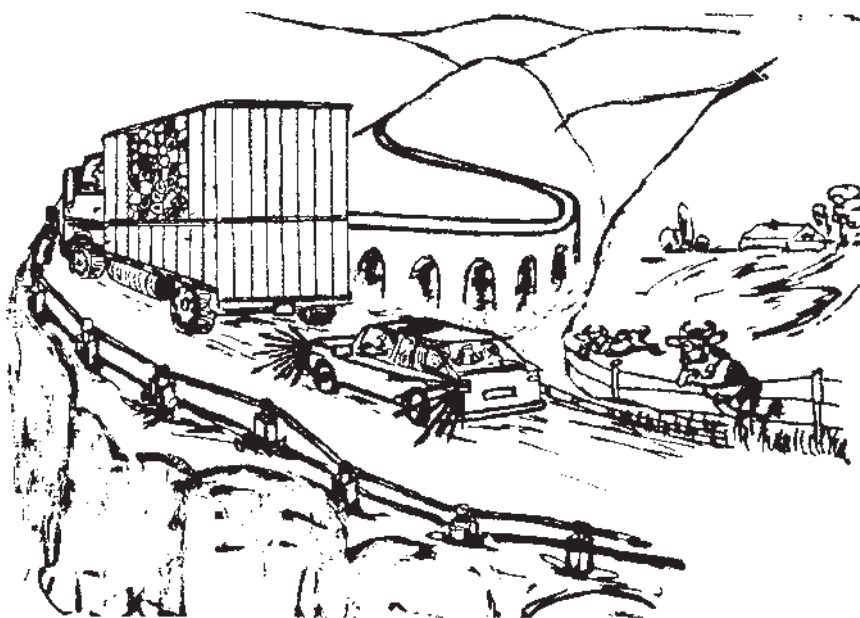


Figure 1.16 The road to Kirchberg. A very important aspect of one-dimensionality is that obstacles cannot be circumvented.

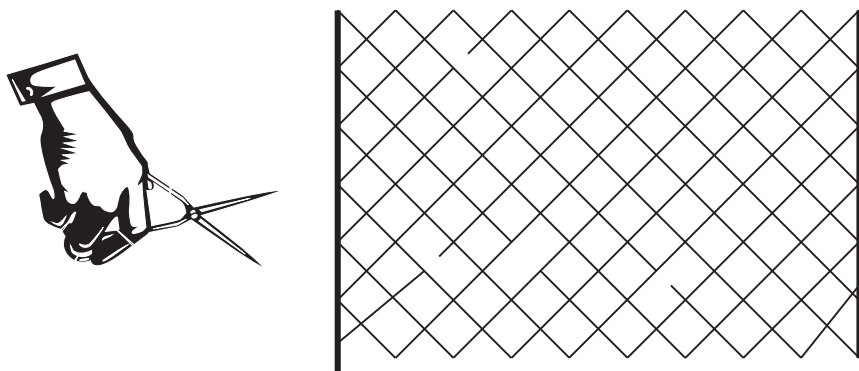


Figure 1.17 Bond percolation demonstration on a two-dimensional grid, where bonds are successively cut in a random way. Source: After Zallen 1983 [19].

transmission probability of the electron traveling its length. What is found is that even for very small variations in the periodic atomic potential, reflections of the electron wave on the wire become large [18].

Another more sophisticated conceptualization of *dimensional restriction* can be made in terms of *percolation*. *Percolation* means macroscopic paths from one side of the sample to the other and the threshold for bond percolation in one dimension is 100%! Such macroscopic paths are necessary, for example, for electrical conduction. The concept of bond percolation is quite different in two dimensions as demonstrated by a grid (Figure 1.17) [19] where bonds are cut at random. In this 2D square lattice, a few cuts yield little change in sample's conduction properties. In particular, the conductivity drops only slightly due to the appearing holes. When 50% of the bonds are cut randomly, no path is left that connects one side of the sample to the other, and the conductivity must be zero. The percentage of intact bonds necessary to establish macroscopic paths is the *percolation threshold*. The higher the dimensionality of the sample, the lower the percolation threshold. For a 1D system the threshold – quite simply – is 100%; if we cut one bond, the sample consists of two disconnected pieces.

Another trivial aspect of 1D systems is the low connectivity. Each atom is connected to two other atoms only: one to the left-hand side and one to the right-hand side. In 3D solids there are connections to neighbors in the back and front as well as to neighbors above and below. Connectivity is a topological concept. Chemists usually speak of the coordination number, the number of nearest neighbors. In a 1D chain the coordination number is 2.

A consequence of the low connectivity of 1D systems is the strong *electron–lattice coupling*. If bonds are completely broken, a 1D system separates into two pieces. Usually complete breaking of bonds does not happen, however. Often bonds are only partially cleaved; for example, only one component of the double bond in the system as in Figure 1.9 or Figure 1.13 is broken. In chemical terms, this means that a bonding state is excited to form an antibonding state. In semiconductor physics it would be described as an electron being lifted from the valence band into the conduction band. Such manipulation of valence electrons is quite common in semiconductors, and it is the first step for photoconductivity

and photoluminescence. In a 3D semiconductor like silicon, the transfer of an electron from the valence to the conduction band creates mobile charge carriers (the electron in the conduction band and the “hole” left behind in the valence band), but it does not change the arrangement of the atoms in the crystal. This is due to the high connectivity of the silicon lattice, where breaking or weakening *one* bond has not much effect. In low-connectivity 1D systems, where each atom is held in place by two neighbors only, each change in bond strength leads to a large distortion of the lattice. In conjugated polymers, the lattice distortion shows a change in bond length when a double bond is partially broken to yield a single bond.

With strong electron–lattice coupling, the electrons moving in the solid creates a large distortion that polarizes the lattice. If the effect is distinct enough, the electrons receive a new name: *polarons* – that is, the charge plus the distortion. Depending on the strength of the coupling and the symmetry of the lattice, there is a variety of quasiparticles resulting from electron–lattice coupling, the most famous of which (and very typical for 1D systems) is the “soliton” [20]. We will have a closer look at solitons and polarons a little later.

An important peculiarity of 1D systems for our discussions is band edge singularities in the *electronic density of states*. As we will see in later chapters, in a solid, electrons cannot have *any* energy they wish (as they could have in vacuum). There are only allowed energy regions (*energy bands*) separated by forbidden gaps – energies they may not take on. The long-range ordering within the system determines these forbidden and allowed energy bands for the carriers. The *density of states* within a band of allowed energies is simply how closely packed together the allowed states are in energy or the number of states per unit energy interval. This density is not constant in a solid. The form of the density of states function depends on the crystal structure, and surprisingly, near the band edge, it reflects the dimensionality of the system. This is shown in Figure 1.18: in three dimensions the density of state function $N(E)$ is parabolic, in two dimensions it

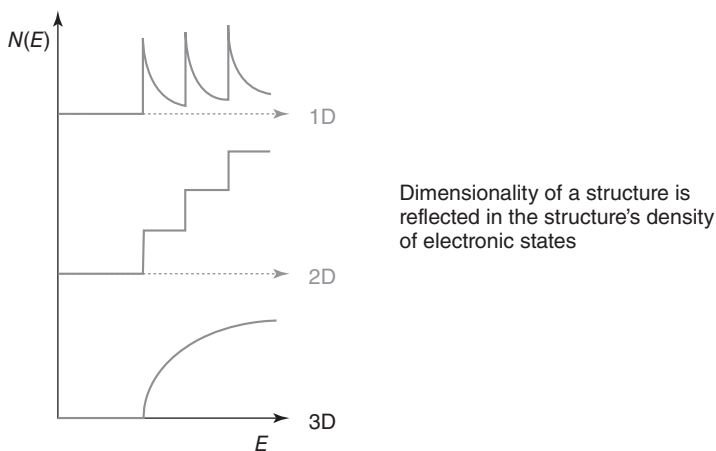


Figure 1.18 Density of states function at the band edge in three-, two-, and one-dimensional electronic systems. Note the singularity that occurs in the one-dimensional case.

is steplike, and in one dimension there is a square root singularity to infinity! In real systems $N(E)$ never reaches infinity, of course, but at least there is a very high density of states.

One-dimensionality also differs from two- and three- dimensionalities in random walk problems. In a higher dimension it is very unlikely that a random walker will return to the place he/she started, whereas in one dimension this happens quite often. Whether or not the random walker comes back to the point of departure is important for discussing the recombination of photogenerated charge carriers and thus for the time constants of transient photoconductivity and of luminescence. Luminescent devices might turn out to be the most important practical applications of 1D metals!

One-dimensional solids are particularly interesting in the context of fundamental studies on phase transitions. In fact, one motivation in the field of 1D conductors arises from the hope of finding the key to high-temperature superconductivity. However, there is a famous theorem of Landau that suggests phase transitions are impossible in 1D systems [21]: long-range order is unstable with respect to the creation of domain walls, because the entropy term in the free enthalpy will always overcompensate the energy needed to form new walls. Whereas phase transitions are impossible, 1D systems might be “close” to a phase transition even at fairly high temperatures. Fluctuations might “anticipate” the phase transition and have already prompted speculation toward some technologically useful properties such as low-resistance charge transport. Perhaps we could allow for “just a little bit” of three-dimensionality and thus obtain a high-temperature superconductor? Organic superconductors are known, but they are closer to two-dimensionality than to one-dimensionality. Their superconducting transition temperatures reach 12 or 13 K (for fullerene even up to 33 K), still far below the recently discovered inorganic oxide superconductors with transition temperatures of 100 K and above [22].

1.6 Summary

In summary, *dimension*, *connectivity*, and *symmetry* show up in many different ways for the solid-state scientist. We note in this chapter that the unusual character of *carbon* with the many structures it is able to make allows us to capture a remarkable number of ways in which a solid can behave in reduced dimension. Basically, the flexibility allows this atom to make a solid in any dimension we might want and with plenty of variants. All of these different allotropes have radically different properties – all based entirely on the organization of the atoms.

As can now be seen, our discussions here will be aimed at introducing both basic and advanced models of solid-state physics in the context of standard chemistry, physics, and materials science. However, *dimensionality* and *topology* will continue to be a unifying language for the materials systems discussed with carbon-based solids as our inspiration. Remember, if you didn’t get the full meaning of everything in *italics* the first time around, don’t worry; we will come back to it again and again.

Synthetic Metals
T_C πs 1d
Kyoto thank we

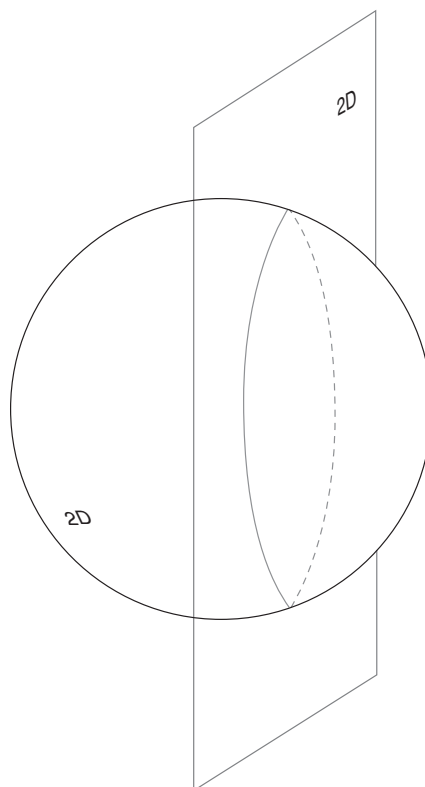
Figure 1.19 Haiku from the ICSM 1986 closing ceremony session in Kyoto [23].

To complete the present chapter however, we reprint in Figure 1.19 a “haiku” that was used during the closing ceremony of the International Conference on Science and Technology of Synthetic Metals in Kyoto [23]. This forum has traditionally focused on the field of conducting polymers, conducting small molecules, low-dimensional organic structures, and similar topics. From it, an international group of scientists formed a community that continues today.

Exploring Concepts

- 1 *Carbon*: The original identification of *carbon*, known at the discovery of metalworking, has been lost to history. Its electronic ground state configuration is [He] $2s^2 2p^2$, and so the outer shell's four electrons have s and p characters. Its melting temperature is 3550°C (6420°F) and boiling temperature is 4827°C (8721°F). And carbon is the world's primary fuel source (energy storage medium). More specifically, the CH_x unit is the basis for most of the *energy-dense fuels* that our planet uses. From gasoline to coal to animal fats, mankind has recognized the extraordinary utility of this sub-compound of carbon and exploited it. Take a little time and compare the energy density (J/kg) of animal fat, oil, coal, a Li-ion battery, and TNT. Remember that the carbon compounds must be oxidized, so when computing the energy released by mass, you must also include the weight of the oxygen to get the true energy density. Many references fail to do this: so don't just go to Wiki.
- 2 *The Euclidean dimension of an object*: Dimension is informally thought of, in physics, as the minimum number of coordinates that are needed to describe any point on or within the object. Likewise, *n-dimensional spaces* extend this idea to include all of the possible coordinate values needed to describe any *n*-dimensional object within the space. However, for our purposes, this isn't quite complete. For example, imagine a ball. It sits in a 3D space, but if confined to the surface of that ball, we are decidedly 2D, and indeed it takes only two coordinates (with reference to some axis set attached to the ball's surface) to describe every point on the ball's surface (longitude and latitude, or θ , φ). If something from a third dimension were to intersect our ball, let's say it is a 2D plane, as seen here, then notice that using the ball's coordinates I could describe only the points of intersection and not anywhere else on the plane (Figure EC1.1). This is similar if I took the point of view of the plane. Moreover, notice that the intersection is a 1D object generally (or 0D in the case of a point). But the set of points that describe the intersection have symmetries reflected in both the flatness of the plane and the spherical nature of the ball. So something else is required to describe the symmetry of the intersection line, and that *something* is related to higher-dimensional objects. This notion is made quantitative in the *topology* and *geometry of manifolds*. So this exercise takes you outside the text a bit. First read up on *topology* and *geometry* and describe how topology is a subdiscipline of geometry.

Figure EC1.1 The apparent lower dimensional intersection between two objects of higher dimension.



How does the *topology* of an object pertain to our discussions here? What is meant by the concepts of *connectedness* and *compactness* in topology? Imagine that we could take a single layer of graphene and connect it to itself along one edge such that it formed a Möbius strip. What do you think this would mean for the electrons in/on the strip?

- 3 *Si and C both form “hybridized” bonding orbitals:* You will learn more about these in the coming chapters. For now however, you can just think of them as orbitals that have very specific directions associated with them. But C is able to allow its bonds to take on a number of different bonding angles (it bends), whereas this is more difficult for Si. Why would you think this might be? What are the ramifications of this for the formation of compounds and crystals? (You may need to journey outside of the text for this one as well.)
- 4 *Euler’s rule:* In simply connected, volumetric polyhedron structures (as in Figure EC1.2), there is a simple rule that must be obeyed before the structure can be constructed and closed using regular polygons (remember *regular polygons* means the 2D structures have many sides but the sides all have the same length).
Now typically, a polyhedron is just one piece. It can’t be made up of two (or more) separate parts stuck together at an edge or a vertex or something. It is

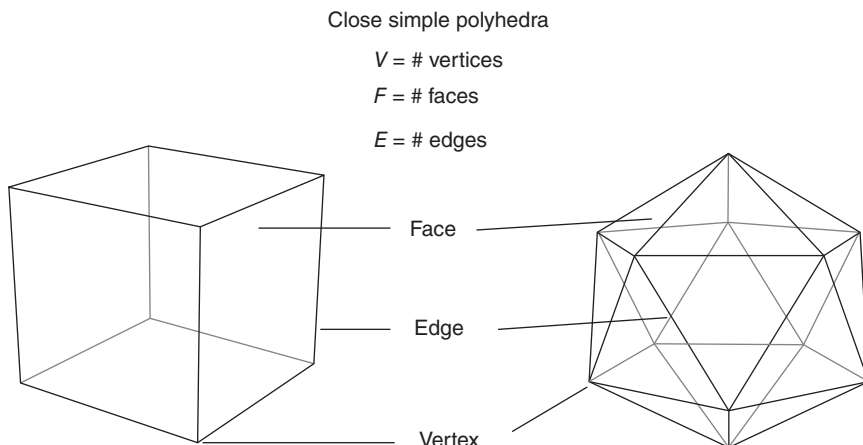


Figure EC1.2 Simply connected polyhedra are simply closed structures with no holes through them.

a “box” and its faces will be made of regularly shaped polygons. But here is the rub. To get that box to close properly without bending the polygons etc., then

$$V - E + F = 2; \text{ (known as the } Euler \text{ rule)}$$

- (a) Using this rule, determine how many pentagons plus hexagons of carbon it will take to construct a C_{60} molecule.
- (b) Is it possible to make a C_{70} ? If so, how many pentagons and hexagons would this require? Draw out what you think this might look like.

- 5** *Fractals and dimension:* Imagine that for any given *Euclidean dimension*, D , we reduce the overall unit of measure by the factor $1/R$. For $R \in I$ we get the schematic shown in Figure EC1.3. The *measure of the object* (that is its length, area, or volume) increases as

$$N = R^D$$

$$D = \text{Log}(N)/\text{Log}(R)$$

This generalized notion of dimension D is known as the *Hausdorff dimension*, and it doesn't need to be an integer as it is in Euclidean geometry. Indeed, in fractal geometries, it is fractional and can be used as an estimate of *roughness*. This idea was eventually applied to the length of coastlines as in Figure EC1.4. In fact, if we assume that the coastline's “roughness” is reproduced at every scale, say, it's *self-similar*, then the processes of halving and then halving again will converge to an estimate of the length of the coastline that is infinite. Thus, such an estimate doesn't make much logical sense. In other words, to describe the coastline, we can't just ask: “how long is it?” The answer to this question doesn't contain complete information. We need something more. L.F. Richardson found a simple way to think of this as seen in Figure EC1.5.

The log–log plot linearity of length estimates in Figure EC1.5 is known as the *Richardson effect*. Mandelbrot used this effectively to define a

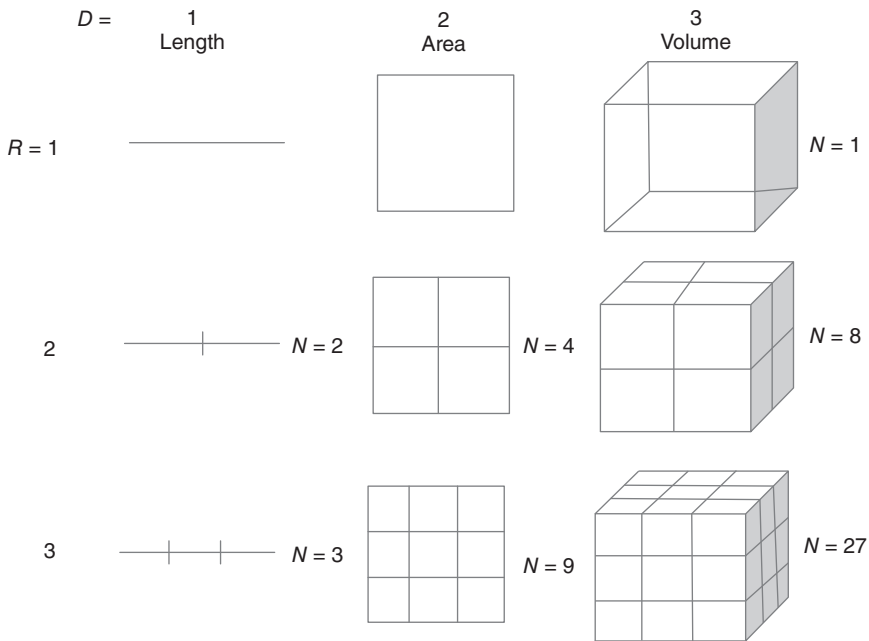
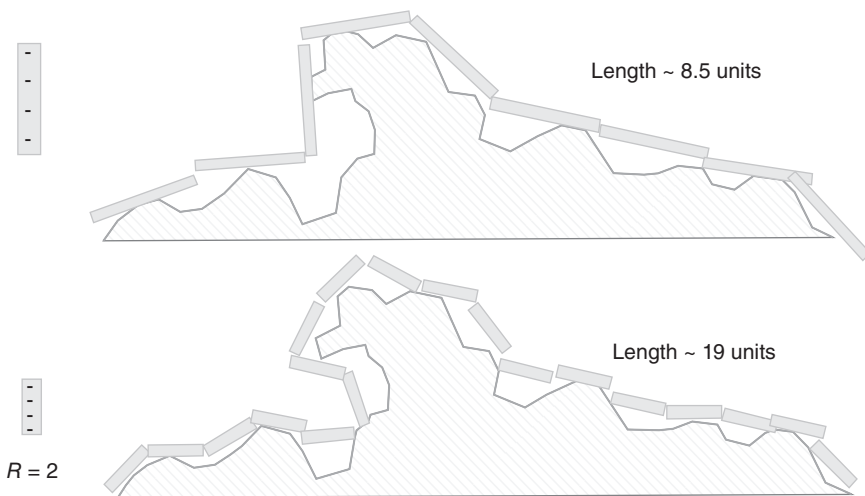


Figure EC1.3 Schematic of the changing unit measure.



What is a coastline's length?
What is its dimension?

Figure EC1.4 Estimating the length of a coastline. Notice the top estimate gives a length of roughly 8.5 rulers in length. Now we halt the length of the ruler. We get a length estimate of the coastline of roughly 19 rulers, not the 17 rulers we might expect. Imagine halving the ruler's length yet again. It is easy to see that more of the "nooks and crannies" of the coastline will be measured, making the estimate require more than twice the last ruler length again.

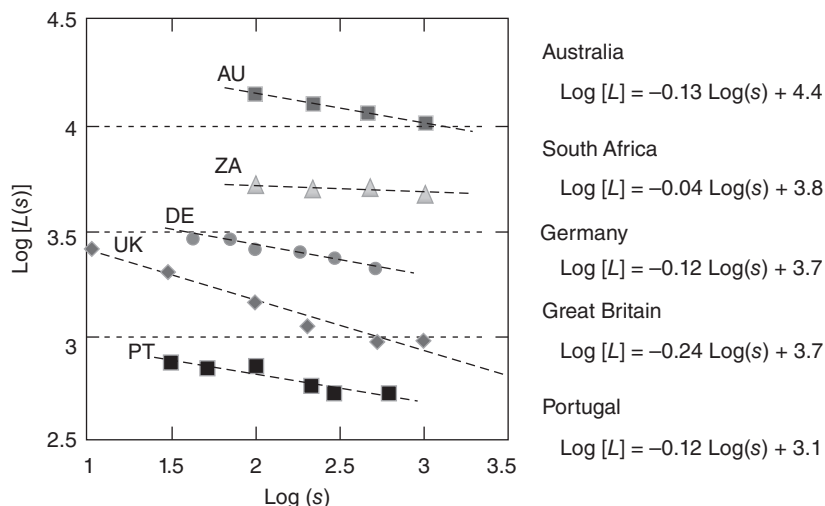


Figure EC1.5 The relationship between the length of coastline estimate and the length of scale used to make that estimate of the coastline is linear on a log–log plot. Indeed, this is true for many naturally occurring structures in the universe, not just coastlines. Of particular interest to us might be polymer lengths, surface areas of rough crystals, and more. Source: Mandelbrot 1983 [3a].

dimensional characteristic to what was being estimated. He assigned the term $(1 - D)$ to the slope. This makes the fitted functions look like $\text{Log}[L(s)] = (1 - D)\text{Log}(s) + b$ where D is the *fractal dimension*.

Notice in the replotted data above that the UK has a $(1 - D) \sim -0.24$. So, $D = 1 - (-0.24) = 1.24$, a fractional value. The coastline of ZA is much smoother. So, the slope above is very nearly zero so $D \sim 1$ (i.e. almost a Euclidean object or a line with a dimensionality of one). Generally, the *rougher* the line, the steeper the slope will be. This yields a larger fractal dimension, as though this highly squiggly line is trying to fill space in a nearly 2D way but doesn't quite make it!

In this exercise you will generate line segments of your own coastline. These are a set of line segments that are self-similar over different length scales.

The Example

The **Koch curve** is constructed conceptually by taking a line segment (the *initiator*) and removing the middle third of the line. The gap is then filled with two line segments that are equal in length to the segments on either side of the gap. This is shown in Figure EC1.6. The new structure is called the *generator*. So, starting with these two structures, the rule says to take each line and replace it with four lines, each one-third the length of the original. Notice that as we do this, the “length” of the curve gets greater and greater until it eventually diverges.

- As we noted the Koch curve length increases with each iteration, until it diverges. So this means we can only deal with it in a treatment as we show for the coastlines above: Figure EC1.5. Estimate the *lengths* for the next

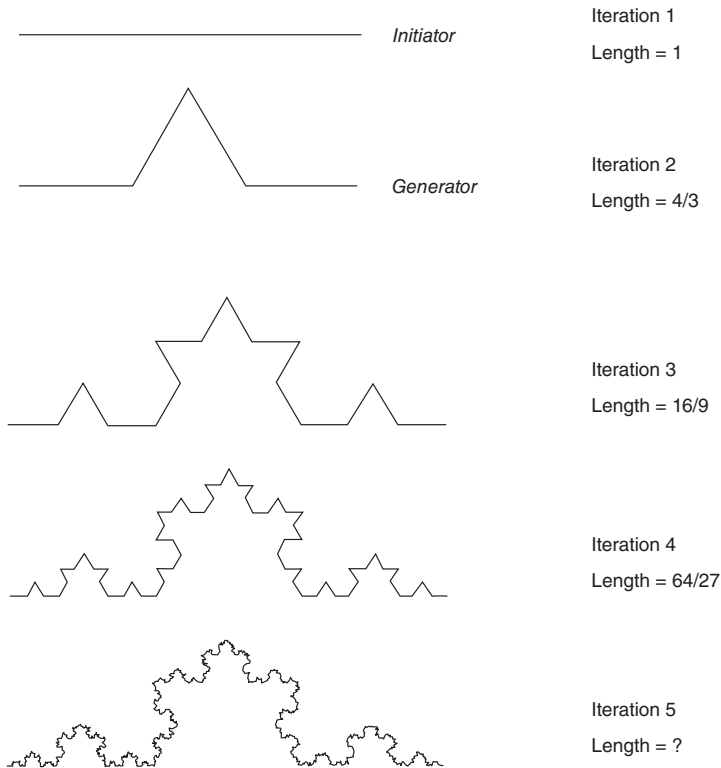


Figure EC1.6 The Koch curve. Starting with the initiator (iteration 1) and the generator (iteration 2), the curve can be continued infinitely.

couple of iterations following the example in Figure EC1.6. Plot them as seen in Figure EC1.5 and then make a determination of the fractal dimension of the Koch curve.

- Write a short *Maple*, *MATLAB*, or *Mathematica* program to produce the Koch curve and estimate lengths for iterations up to 20 or so. How fast is the length diverging? How fast does the fractal dimension converge to a limiting value and how close was your estimate in (a)?
- Now let's see how to use this and why we have placed this in a solid-state book. Go to a local atomic force microscope (AFM). Get a sample of fractured glass or metal of appropriate size. Image this sample observing the roughness in the image and in individual line scans (see user's manual for your machine). The software of most AFMs allow for a roughness analysis to be made; you just hit a key and it gives a number. There are a number of different ways to define and calculate this roughness, but generally the machine will determine the mean or average variation from a horizon line defined by the image itself and call this the roughness. However you might suspect that there is some relationship between this number and that of the fractal dimension, and with a few small limitations and caveats, there is. Using *MATLAB* or one of the other symbolic math programs, write

out a code to load one of the line scans into the program and then overlay line segments to determine length in methods similar to that of the above Richardson plot. From this determine the fractal dimension.

Now change the imaging conditions including the size of the scan area, the speed of scanning, etc. (we are assuming you know what an AFM is here of course). Repeat what you have just done. Is the answer different? Yes! Of course it is. But do you know why? How many scales would I need to scan over to ensure that I have a reasonable correlation between what we will call surface roughness and fractal dimension?

Note to the reader about our problem sets: Ever notice how some texts end their chapters with *problem #1* derive equation 2.7... *problem #7* repeat problem #4 for all these different lattice parameters... and on they go. Well, our problems don't work that way. Following the lead of great works like Kittel, we assume that our readers are living and breathing their desire to become true solid-state physicists. So, they are not opposed to reaching outside of the text to understand a concept through a reference or performing an experiment or two to test our conjectures. Occasionally easily accessed references just don't provide enough discussion, and so we walk you through that concept in the problem. In other cases, gems are lying upon the ground waiting to be read and appreciated. We encourage the reader to try *all* of our problems first alone and then within study groups and with their instructors. They are not homework, they are home entertainment, and they are opportunities to go well beyond what we have covered in the text.

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