One-Dimensional Metals

Conjugated Polymers, Organic Crystals, Carbon Nanotubes and Graphene

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Introduction

1.1
Dimensionality

Dimensionality is an intellectually very appealing concept and 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” [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?” (Figure 1.1).

This fictitious dialog 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 also a logical basis for this difference [3]. In general, the quantity that changes with time and in which physicists are interested, is one property of an object. The object in question is imbedded in space, usually in three dimensions. Objects may be very flat, such as flounders, saucers, or oil films with length and width much greater than their thickness. In this case, thickness can be negligible. Such objects can be regarded as (approximately) two dimensional. But, in another example, the motion of an object is restricted to two dimensions like that of a boat on the surface of a sea (hopefully). According to our everyday experience, one- and two-dimensional objects and one- and two-dimensional motions actually seem more common than their three-dimensional counterparts, and hence low-dimensionality should not be spectacular. Perhaps that is the reason for the introduction of noninteger (“fractal”) dimensions [4]. 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 as both objects and the space in which objects of physics exist, for example, various silicon single crystals can be compared with

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Figure 1.1 Simultaneously with Herbert Marcuse's book "One-Dimensional Man" [1], which widely influenced the youth movement of the 1960s, Little's article on "Possibility of Synthesizing an Organic Superconductor" [2] was published, motivating many physicists and chemists to investigate low-dimensional solids.

each other, or they can be considered as the space in which electrons or phonons move. On one hand, the layers of a crystal, for instance, the *ab*-planes of graphite, can be regarded as two-dimensional objects with certain interactions between them that extend into the third dimension. On the other hand, these planes are the two-dimensional space in which electrons move rather freely. Similar considerations apply to the (quasi) one-dimensional hydrocarbon chains of conducting polymers.

1.2
Approaching One-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" 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 one dimensional (Figure 1.2). How thin will it have to be for being truly one dimensional? This depends a little on exactly what property of the object is desired to express low-dimensional behavior. Certainly, thin compared to some microscopic parameter associated with that property. For example, for one-dimensional electrical transport properties, the object 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.

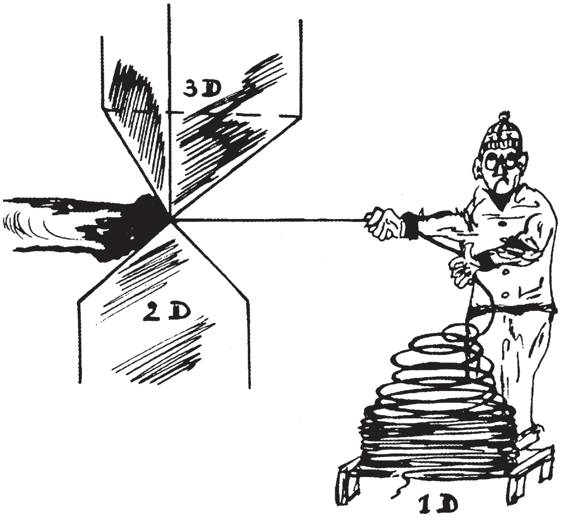

Figure 1.2 An "external approach" to one-dimensionality. A man tries to draw a wire until it is thin enough to be regarded as one-dimensional. Metallic wires can be made as thin as 1 μm in diameter, but this is still far away from being one-dimensional. (By lithographic processes, semiconductor structures can be made narrow enough to exhibit one-dimensional properties.)

But, does the wire have to be drawn so extensively to finally become a monatomic chain? Well, the Fermi wavelength becomes relevant when discussing the eigenstates of the electrons (we learn more about the Fermi wavelength in Chapter 3). 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):

$$\Delta E_L = \frac{h^2}{2m\left(\frac{\pi}{L}\right)^2}, \tag{1.1}$$

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. The Fermi level is the highest occupied state (at absolute zero). The wavelength of the electrons at the Fermi level is called the Fermi wavelength. If the size of the box is just the Fermi wavelength, only the first eigenstate is occupied. If the energy difference to the next level is much larger than the thermal energy ($\Delta E_\mathrm{L} \gg kT$), then there are only completely occupied and completely empty levels and the system is an insulator. 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 $\Delta E_\mathrm{radially} \gg kT$ whereas $\Delta E_\mathrm{lengthwise} \ll kT$.

If there are only very few electrons in the box, the Fermi energy is small and the Fermi wavelength is fairly large. For *real* materials, these are the electrons that

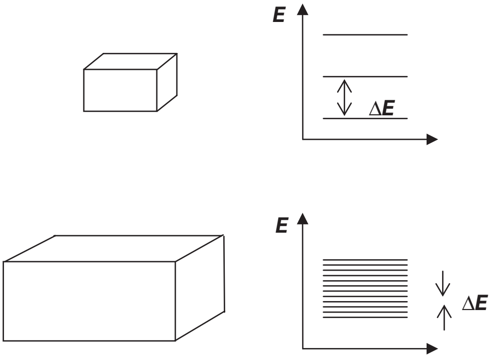

Figure 1.3 Electrons in small and large boxes and energy spacing of the eigenstates.

can participate in bonding–antibonding orbitals. This is the case for semiconductors at very low doping concentrations. Wires of such semiconductors are already one dimensional if their diameter is of the order of approximately hundreds of angstroms.

Such thin wires can be fabricated from silicon or from gallium arsenide by lithographic techniques and effects typical for one-dimensional electronic systems have been observed experimentally [5]. Systems with high electron concentrations have to be considerably thinner if they are to be one dimensional. It turns out that for a concentration of one conducting electron per atom, we really need a monatomic chain!

Experiments on single monatomic chains are very difficult, if not impossible, to perform. Therefore, typically, a bundle of chains rather than one individual chain is used. An example for such a bundle is the polyacetylene fiber, consisting of some thousands of polymer chains, closely packed with a typical interchain distance of 3–4 Å. Certainly, there will be some interaction between the chains; however, in case of small interchain coupling, it can be assumed that just the net sum of the individual chains determines the properties of the bundle (Figure 1.4) and the experiment becomes one of an ensemble of one-dimensional chains.

Another method of geometrical shaping employs surfaces or interfaces (Figure 1.5). The surface of a silicon single crystal is an excellent two-dimensional system and there are various ways of confining charge carriers to a layer near the surface. In fact, the physics of two-dimensional electron gases is an important part of today's semiconductor physics [6] and most of the two-dimensional electron

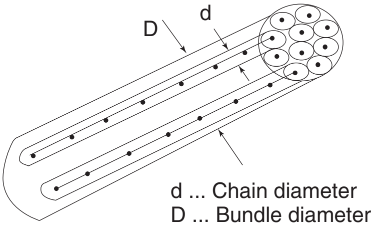

Figure 1.4 Experiments on individual chains are difficult to perform. But bundles of chains are quite common, for example, fibers of polyacetylene.

Figure 1.5 Crystal surface are excellent two-dimensional systems. The man above tries to improve the crystal face by mechanical polishing. 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.

systems are confinements to surfaces or interfaces. The most fashionable effect in a two-dimensional electron gas is the quantized Hall effect or von Klitzing effect [7]. A one-dimensional surface, that is, the edge of a 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 one-dimensional electronic system since electrons can be forced into motion along specific paths defined by the crystal and the field. In fact, reducing von Klitzing's sample to "edge channels" is one way of explaining the von Klitzing effect [8].

The "internal approach" to one-dimensional 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 other two perpendicular directions, a nearly one-dimensional 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 the existing solids that could be regarded as (quasi) one dimensional. Some anisotropic solids are compiled in the next chapter of this textbook. 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 in Chapter 3, 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 as well.

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

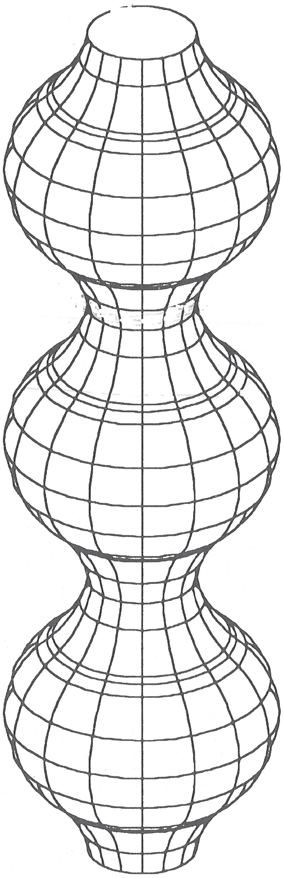

Figure 1.6 Open Fermi surfaces, analogous to merged soap bubbles, as a criterion of low-dimensionality. The Fermi surface belongs to a solid that is essentially two dimensional. The solid will have no electronic states contributing to electrical conductivity along the axial direction but will easily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

1.3
Dimensionality of Carbon Solids

Silicon is outstanding among solids [9]: it is the most perfect solid producible – 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 has largely influenced the vocabulary of solid-state physics (probably apparent by a style analysis of this text too). 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 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 three-, two-, one-, and zero-dimensional solids. This is related to the fact that carbon has the ability to form single, double, and triple bonds. This characteristic feature of carbon sets it aside from silicon in another important way, that is, it leads to biology.

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 ($a = 5.43$ Å in silicon and 3.56 Å in diamond), and the energy gap between valence and conduction bands is larger in diamond: 5.4 eV, compared to 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 of raw material change the final price of electronic equipment only slightly, some people believe in diamond as the semiconductor of the future. Silicon is typically used with added dopants to modify its

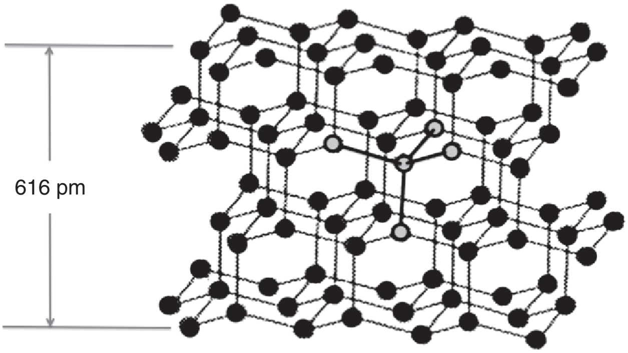

Figure 1.7 Diamond lattice.

electronic behavior. Doping diamond has proven to be far more difficult however, and must be better understood before the realization of high-quality diamond electronics.

"Semiconductors" will often be mentioned in this textbook although the title promises metals to be the main subject. The reason stems from the fact 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

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 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 Å 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.

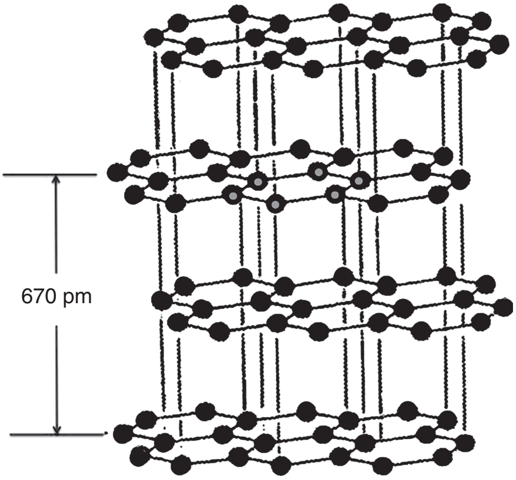

Figure 1.8 Graphite lattice.

Diamond is a semiconductor and graphite is a metal. 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 three-dimensional graphite [10]. Theoretically, it seems possible [11], 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 two dimensional, 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 two-dimensional sheet "samples" the three-dimensional 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 – a Berry's phase, which comes from the geometrical intersection of the two- and three-dimensional worlds. Graphene has been studied extensively over the last few years and transport in graphene led to the 2010 Nobel Prize in physics [12]. By numbers: Density of graphene is $0.77\ \mathrm{mg/m^2}$, its breaking strength is $42\ \mathrm{N/m}$, electrical conductivity is $0.96 \times 10^6\ \Omega^{-1}\ \mathrm{cm}^{-1}$, 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, Polyene

As we have already pointed out, carbon has this amazing ability to bond to itself in many ways. Using double bonds, one can easily construct – at least on paper – one-dimensional carbon: Figure 1.9 shows a monatomic carbon chain. This substance is called *cumulene*, the name referring to cumulated double bonds. From organic chemistry, it is well known that double bonds can be "isolated" (separated by many single bonds), "conjugated" (in strict alternation with single bonds), or "cumulated" (adjacent). Cumulene has not been synthesized, but using the principles of quantum chemistry it can be predicted whether cumulene would be stable or would rather transform into *polycarbyne*, an isomeric structure in which triple bonds alternate with single bonds. Polycarbyne is shown in Figure 1.10. The odds are for polycarbyne being the more stable molecule. Polycarbyne occurs in interstellar dust and in trace amounts within natural graphite but is not yet available for performing experiments [13].

$$\text{- - -}\ \mathrm{C{=}C{=}C{=}C{=}C{=}C}\ \text{- - -}$$

Figure 1.9 One-dimensional carbon: cumulene.

$$-\mathrm{C{\equiv}C}-\mathrm{C{\equiv}C}-\mathrm{C{\equiv}C}-$$

Figure 1.10 One-dimensional carbon: polycarbyne.

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

As a brief note on naming conventions: in organic chemistry, 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 case is ethylene, $H_2C{=}CH_2$. Here the monomer contains a double bond, but during polymerization the double bond breaks to link the neighboring molecules.) Polyanes are insulators and of little interest in the context of this textbook. (Insulators are large band-gap semiconductors. Because of the large band gap, 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. Chapter 5 is concerned with conducting polymers, and will discuss polyacetylene in greater detail.

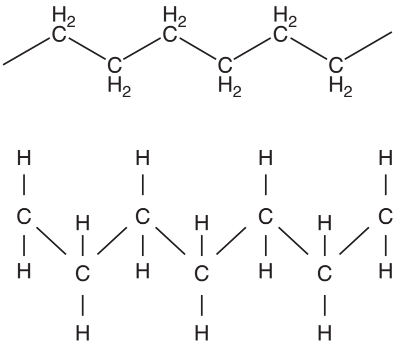

Figure 1.11 Polyethylene, shown at the top as we might imagine the polymerization of ethylene, shown at the bottom as we might imagine the arrangement of bonding.

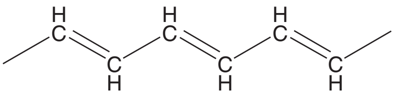

Figure 1.12 Polyacetylene, the prototype polyene, the simplest polymer with conjugated double bonds.

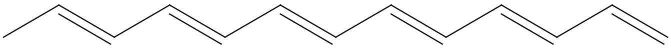

Figure 1.13 Polyacetylene using a simplified notation.

1.3.4

Zero-Dimensional Carbon: Fullerene

If we work our way down in dimensionality from *body-diamond* to *plane-graphite and graphene* to *lines-polymers,* we will finally end up at the *point* as a zero-dimensional object. Do zero-dimensional solids exist outside of the obvious (the atom)? In semiconductor physics, the "quantum dot" is well known [14]. Historically, this is a small disc cut out of a two-dimensional electron gas. It is small compared to the Fermi wavelength, so that the electrons are restricted in all three dimensions of space (the one-dimensional analog to a quantum dot is often called "quantum wire"). Following the discussion in Section 1.2, a quantum dot is a zero-dimensional object. The present state of the art is to fabricate quantum dots containing more than one but less than ten electrons. Because of the low electron concentration in semiconductors, such quantum dots can exhibit quite large diameters, up to several hundred angstroms. More recently, quantum dots have been fabricated as chemically assembled nanoparticles, wherein the structure defines the confinement. Metal nanoparticles of Au, Ag, Cu, and so on, have been created using a variety of chemical synthesis routes and confinement of the electrons occurs at particle diameters of only a few nanometers. Similarly, quantum dots made from semiconductor materials, such as Si, Ge, and compounds such as CdS, CdSe, PdS, and so on, 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 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, and so on, 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

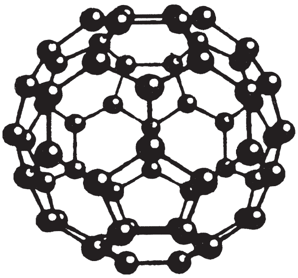

Figure 1.14 A fullerene molecule. This is an example of a C_{60}, but much larger cages can be made.

about 10 Å, 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! (For more details on π-electrons, see Chapter 5.) In other words, there are 60π-electrons in a fullerene ball of 10 Å diameter, compared to some five electrons on a 100 Å 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 and 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, such as superconductivity [16], photoconductivity, and electroluminescence [17]. Figure 1.14 shows the graphic representation of a fullerene mini-solid, and Figure 1.15 schematically indicates the fullerene macro-solid.

1.3.5
What about Something in between?

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 Å, we refer to the object as a "carbon nanotube." For such an object, the electron wavefunction is confined to box-like states around the circumference. Along the axis of the tube, the electrons move in essentially a one-dimensional 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 three dimensional 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 one-dimensional system, it also has a "little more." It is clearly not quite two

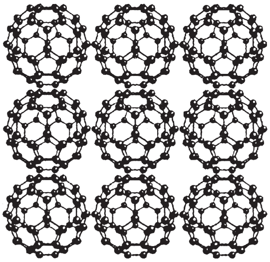

Figure 1.15 The fullerene crystal lattice: "fullerite." These compounds have a rich chemistry. They can be doped by placing atoms between the balls, inside the balls, and so on.

dimensional, however. For such systems, the “topology” of the dimension must be considered. We learn more about carbon nanotubes in the following chapters.

1.4
Peculiarities of One-Dimensional Systems

Theory predicts that *strictly* one-dimensional systems will behave very unusually, so in this context the word “pathological” is often used. Real systems appear less pathological than predicted because they are only *quasi* and not strictly one-dimensional. Real systems differ from ideal systems by having chains of finite rather than infinite length. In addition, the chains show imperfections such as kinks, bends, twists, or impurities. They are contained in an environment other than perfect vacuum, with neighboring chains at a finite distance and thus a nonzero interaction between them.

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 one-dimensional 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 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 this fact 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

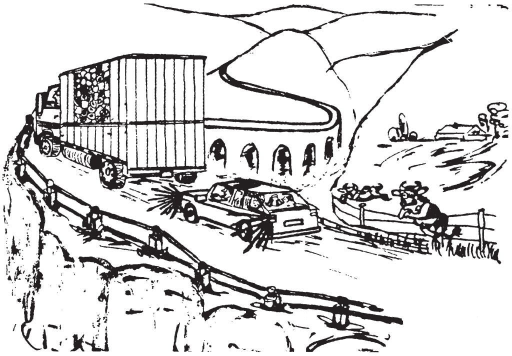

Figure 1.16 A very important aspect of one-dimensionality is that obstacles cannot be circumvented.

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 two-dimensional square-lattice, a few cuts yield little change in sample's conduction properties. In particular, the conductivity drops only slightly due to appearing holes. When 50% of the bonds are cut randomly, no path is left which 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 one-dimensional system, the threshold – quite simply – is 100%: if we cut one bond, the sample consists of two disconnected pieces.

Another – trivial – aspect of one-dimensional 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 three-dimensional 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 one-dimensional chain, the coordination number is two.

A consequence of the low connectivity of one-dimensional systems is the strong "electron–lattice coupling." If bonds are completely broken, a one-dimensional system separates into two pieces. 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 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 three-dimensional semiconductor, such as 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 one-dimensional systems, where each atom is held in place by two neighbors only, each change in

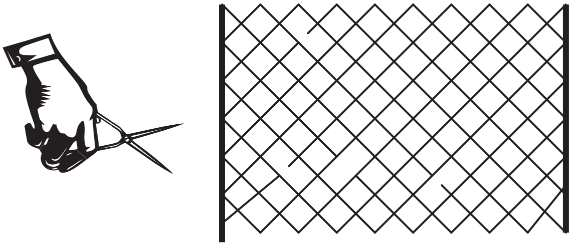

Figure 1.17 Bond percolation demonstration on a two-dimensional grid, where bonds are successively cut in a random way. (After Zallen [19].)

bond strength leads to a large distortion of the lattice. In conjugated polymers, the lattice distortion shows in 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 create 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 quasi-particles resulting from electron–lattice coupling, the most famous of which (and very typical for one-dimensional systems) is the "soliton" [20]. We have a closer look at solitons and polarons in Chapter 5.

Another peculiarity of one-dimensional systems is band-edge singularities in the electronic density of states. We learn more about electrons in a solid in Chapter 3, but here we note already that in a solid, electrons cannot have any energy (as they could have in vacuum). There are allowed regions ("bands") separated by forbidden gaps and this is determined by the long-range ordering within the system. The density of states within a band, that is, the number of states per energy interval is not constant. The form of the density of states function also depends on the crystal structure. Near the band edge, it reflects the dimensionality of the system. This is indicated in Figure 1.18: in three dimensions, the density of state function $N(E)$ is parabolic; in two dimensions, it is step-like; 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. If the Fermi level is within such a region, high-temperature superconductivity is favored (cf. A15 superconductors, Section 2.1).

One-dimensionality also differs from the other dimensionalities in random walk problems. In a high dimension, it is very unlikely that the random walker will return to the place he started from, 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 one-dimensional metals!

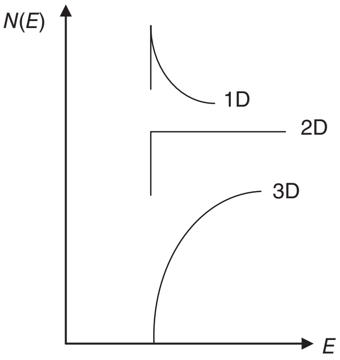

Figure 1.18 Density of state function at the band edge in three-, two-, and one-dimensional electronic systems. Note the singularity which occurs in the one-dimensional case.

One-dimensional solids are particularly interesting in the context of fundamental studies on phase transitions. In fact, much of the motivation in this field arises from the hope of finding the key to high-temperature superconductivity. There is the famous theorem of Landau that phase transitions are impossible in one-dimensional 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. But whereas phase transitions are impossible, one-dimensional 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, for instance, 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]. Chapter 7 is devoted to organic superconductors.

In Chapter 4, we discuss the Peierls transition. This is a transition from a metal at high temperatures to a semiconductor or insulator at low temperatures. It is driven by the strong electron–phonon coupling in one-dimensional systems and related to the formation of conjugated double bonds in conducting polymers, in this case referring to the strict alternation of double and single bonds with different bond lengths rather than equidistant "one and a half bonds." The charge density waves (Chapter 8) can be regarded as an "incomplete" or itinerant Peierls transition.

Before discussing these phenomena, we focus on the concepts of solid-state physics in greater detail (Chapter 3), after enjoying a "sight-seeing trip" to some of the most attractive one-dimensional substances in Chapter 2.

Chapter 9 will give an introduction to the field of molecular electronics, which in many aspects is linked to low-dimensional solids. At first glance, it might be proposed to use the polymer chains of a one-dimensional metal as ideal molecular wires. This is not very realistic. However, the strong electron–phonon coupling in one-dimensional systems (and, in particular, in organic systems) will lead to a better localization of excitations and thus might be applied to denser packing of information (i.e., to smaller devices and to higher integration). Nanoscale-molecular electronic devices certainly are applications of the "distant future." But there are also near future and even present-day applications of one-dimensional solid-state systems. A survey of this, Chapters 10 and 11, concludes this textbook. To complete this introductory chapter, we reprint in Figure 1.19 a "haiku," which was used during the closing ceremony of the International Conference on Science and Technology of Synthetic Metals in Kyoto [23].

Synthetic metals
T_C $\pi\sigma$ 1d
Kyoto thank we

Figure 1.19 Haiku from the ICSM '86 closing ceremony session in Kyoto [23].

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