1 The Geometry of Nanoscale Carbon

Since later chapters will cover the synthetic, electronic and transport properties of carbon nanostructures in depth, here we take a different point of view and focus on the theory of their structure and geometry. The well-defined covalent bonding geometries of graphitic carbon lead to a simple set of geometrical rules that relate the global shape of a carbon nanostructure to the types of carbon rings within it.

1.1 Bonding

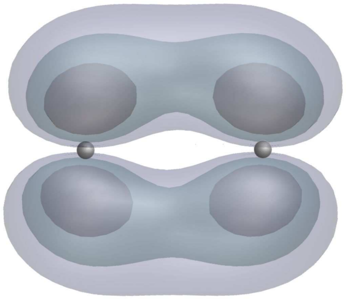

Figure 1: Charge density of a carbon dimer π state.

Carbon is an unusual element. The isolated carbon atom has filled $1s$ and $2s$ states and two electrons in the $2p$ state for a configuration of $(1s^2 2s^2 2p^2)$. Since carbon is a first-row element, the atom is very small and the Coulomb potential felt by the valence electrons is correspondingly high (remember the Coulomb potential energy varies as $1/r$). When carbon atoms are assembled into a larger structure, the potentials from nearby atoms perturb the $2s$ and $2p$ atomic orbitals and create bonding, nonbonding, and antibonding molecular orbitals formed from linear combinations (i.e. sums and differences) of the $2s$ and $2p$ states. Bonding occurs when the charge density of the electronic wavefunction occupies favorable areas, wherein the attractive atomic potentials of neighboring atoms overlap. Normally, the bonding orbitals between neighboring atoms pile up electron charge in the space that lies directly between the atoms, since this is the region where the attractive atomic potentials overlap most strongly. Such bonds are called σ states. However, for carbon, an accident of the fundamental constants (i.e. the mass of the electron, Planck's constant, the charge of an electron) implies that two neighboring atoms can also bond strongly by piling up charge in the regions above and below the line of intersection between the atoms, the so-called π states (Figure 1). Because carbon can bond "sideways" in this manner, using the p states that point perpendicular to the line connecting the neighboring atoms, it can form highly anisotropic and stable two-dimensional layered structures.

The lowest-energy state of elemental carbon at ambient pressure and temperature is graphite (Figure 2). Graphite consists of individual graphene layers, each composed of interlinked hexagonal carbon rings tightly bonded to each other, stacked loosely into a three-dimensional material.

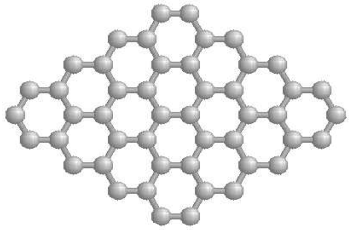

Figure 2: Graphene

Within a single graphene layer, oriented in the x-y plane, each carbon atom is tightly bonded to three neighbors within a plane; these planes are then very weakly bonded to each other. The in-plane sp^2 bonding is best understood by first considering graphene, a single layer of graphite. The $2s$, $2p_x$ and $2p_y$ orbitals are recombined to form three new linear superpositions (thus the name sp^2). These three new linear combinations form three lobes of charge reaching outward from the carbon atom at 120 degree angles to each other, all within the x-y plane. These lobes form σ bonds to three neighboring carbon atoms. The leftover $2p_z$ orbital, which points perpendicular to the plane of the sp^2 bonds, overlaps with $2p_z$ orbitals on neighboring atoms to form an extended sheet-like bonding state that covers the upper and lower surfaces of the graphene sheet. The $2p_z$ orbitals of neighboring atoms overlap most effectively if they point in the same direction; therefore the sheet has its lowest energy when it is perfectly flat.

Since the overlap of the atomic potentials is strongest along the line between the atoms, the electronic bands arising from the σ states are lower in energy than those arising from the π states. In fact, the π states, plus their antibonding cousins the π^* states, span the Fermi energy. (The antibonding π^* states are just higher-energy combinations of the same $2p_z$ orbitals. They are unoccupied in a pure graphene sheet). The interactions between the layers are very weak, arising from a combination of van der Waals interactions and electron delocalization in the $\hat{z}$ direction. The subtleties of the electronic overlap in the $\hat{z}$ direction and the exact patterns of stacking for graphite will not be covered here.

Normally, strong atomic potentials and covalent bonding imply the existence of a large bandgap, since strong potentials give well-separated atomic energy levels and large separations between the electron bands. However, nature again conspires to make carbon in the graphene structure special: sp^2-bonded atoms prefer three-fold coordination, so they naturally assemble into hexagonal sheets with two atoms in each unit cell. The potential arising from this structure can't distinguish between the π and π^* states at the Fermi level, so they remain equal in energy and these two bands formed from the $2p_z$ orbitals actually touch each other at E_{Fermi}. Since the system can't lower its energy by creating a bandgap, it does the next best thing and instead necks down the highest-energy filled electron bands (the π states) to the smallest possible number of states, a set of isolated single points, at the Fermi energy. In addition, the carbon atoms draw closer together to increase the interatomic overlap. This overlap spreads out the π and π^* bands over a wide range of energy and thereby pushes the occupied π states as low as possible in energy. As a side effect, the velocity of the electrons at the Fermi energy becomes rather large. A graphene sheet lives on the boderline between metallic and semiconducting behavior: it is both a metal with a vanishing Fermi surface and a semiconductor with a vanishing bandgap. The chapter by J. Fischer describes this electronic structure in more detail.

Carbon's neighbors to the right and left in the first row of the periodic table (boron and nitrogen) can also make strong π bonds. However, only carbon occupies the favored position of having exactly four electrons and requiring exactly four bonds to make a closed shell; therefore only carbon is stable as an extended covalently-bonded elemental two-dimensional structure. Nitrogen, in contrast, requires only three bonds, so can form a highly stable triple-bonded N_2 molecules in preference to an extended sheetlike stucture. Boron, in contrast, lacks the fourth electron that stabilizes the π-bonded sp^2 sheet; instead it forms complex structures with multi-centered bonding.

Question: Describe how one could make extended sp^2-based solids from boron and/or nitrogen by combining more than one element into the structure. How might one expect this material to differ from graphene?

1.2 Dimensionality

What exactly do we mean that a graphene sheet is two-dimensional? Like anything else, it's really a three-dimensional object, with a non-zero extent in the x, y and z directions. The *effective* two-dimensionality of graphene is fundamentally a question of quantum mechanics and energies. For directions within the sp^2 plane, the structure extends long distances; therefore one can form quantum states for electrons with many different finely-grained wavelengths, very closely spaced in energy. It's easy to squeeze in one more node into the wavefunction when one has so much space. However, perpendicular to the plane, the graphene sheet is quite thin, about 0.3 nanometers. Adding another node to the wavefunction in this direction (which means essentially, creating an excitation to the 3p atomic level) requires putting a very high curvature into the wavefunction and consequently implies a very large energy, far beyond the thermal energies available.

The ability of carbon to form these highly stable effectively two-dimensional structures is fundamental to their great promise in nanoscience and technology. Why? Because we live in a three-dimensional world, so we can distort this two-dimensional graphene sheet in the third dimension to form a very rich family of structures. The energy cost to perform these distortions is relatively small: graphite is a single atomic layer, so it can be bent without changing the in-plane bond lengths significantly. Since the direction of bending is perpendicular to the direction of the in-plane bonds, the energy to create a bending distortion is quadratic in the magnitude of the distortion, rather than linear, as it would be if the bond lengths were forced to change. *Note to experts: this is why the acoustic phonon of graphite that is polarized in the $\hat{z}$ direction has a nearly quadratic dispersion at low wavevector.*

Question: Show that bending a graphite sheet perpendicular to the plane of the σ bonds changes the carbon-carbon bond-length by an amount that is quadratic in the upwards shift of a carbon atom away from the original flat plane.

How can we exploit the third dimension to bend and distort a two-dimensional graphene sheet into interesting structures? First off, to be stable, any dangling bonds at the edges of such a distorted sheet must be eliminated. There are two ways to do this: either cap off dangling bonds with chemical groups such as hydrogen atoms or wrap the carbon structure around onto itself so that it forms a closed sheet with no edges. In the first case, one obtains an open structure; in the second, a closed structure. We begin with a discussion of the closed structures, known as fullerenes, since the geometrical rules that govern that situation can be easily extended to consider open structures as well.

1.3 Topology

The fundamental requirement in a closed graphene-like structure is that every carbon atom have three bonds to neighboring atoms, and that the entire structure fold back on itself without any dangling bonds. These conditions are questions of topology, meaning the connectivity of an interlinked network of bonds. Topology establishes the constraints that must be satisfied when sp^2-bonded atoms bond together seamlessly into a closed structure. When analyzing the topology, we can imagine the bonding network to be infinitely deformable, so long as we don't break any bonds. For the moment forget what you might know about bond angles and bond distances; topology concerns itself only with the presence or absence of a connection between atoms.

Think of any closed sp^2-bonded carbon structure as a polyhedron, where each carbon atom is a vertex, each bond is an edge, and each closed ring of atoms forms a face. The condition that this polyhedron close back onto itself imposes a universal mathematical relationship between the number of edges, faces and vertices. To find this relationship, we can begin with the simplest possible closed polyhedron: a tetrahedron, and successively extend the structure by adding new atoms. Remember that we're concerned for now only with topology: carbon atoms don't really form tetrahedra, since the bond angle distortions are too great. Nevertheless, the tetrahedron is the natural starting point for the mathematical construction of larger, more chemically plausible carbon polyhedra. The tetrahedron has four faces ($F = 4$), four vertices ($V = 4$), and six edges ($E = 6$). Notice that $F + V = E + 2$. We can extend the tetrahedron to form more complex polyhedra in any of the three ways depicted below.

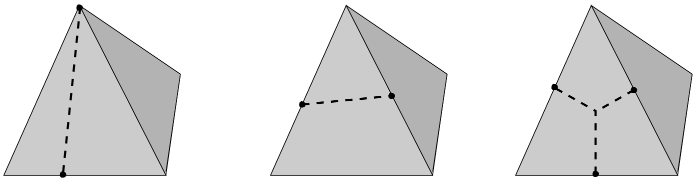

Figure 3: Euler's rule in a tetrahedron.

Adding the bond connecting a vertex and an edge (left-hand side of figure 3) creates one new vertex, one new face, and two new edges. Alternatively, adding the thick line connecting two edges (middle) creates two additional vertices $V \to V + 2$, one additional face $F \to F + 1$ and three additional edges $E \to E + 3$. Finally, adding a new vertex in the middle of a face and connecting it to n edges and m vertices (right-hand side) creates $n + 1$ new vertices, $n + m - 1$ new faces, and $2n + m$ new edges. By successive action of these operations we can construct any polyhedron, starting from the tetrahedron. How can we convince ourselves that we can make any polyhedron this way? Just think in the reverse: start from the polyhedron that you want to reach, and successively remove vertices and bonds; eventually only four vertices will remain, and the structure at that point must be a tetrahedron. *Note to experts: The operations that attach a new bond* *to a vertex are not relevant to sp^2-bonded structures, since they produce atoms with more than three nearest neighbors. However, they are necessary to create an arbitrary polyhedron, and including them here doesn't change any of the rules derived below.* Notice a very interesting fact: each of the operations

Left	Middle	Right
$V \rightarrow V+1$	$V \rightarrow V+2$	$V \rightarrow V+n+1$
$F \rightarrow F+1$	$F \rightarrow F+1$	$F \rightarrow F+n+m-1$
$E \rightarrow E+2$	$E \rightarrow E+3$	$E \rightarrow E+2n+m$

preserves the validity of the relation $F+V=E+2$ which we wrote down initially for the tetrahedron.

Actually, we are missing one more subtle operation: we could deform a sufficiently large polyhedron by bending it around onto itself and fusing together two faces, both which have the same number of sides, call it s, to give a donut-like shape with a hole in the center. This operation eliminates two faces $F \rightarrow F-2$, s edges $E \rightarrow E-s$, and s vertices $V \rightarrow V-s$. To retain our relationship $F+V=E+2$, we must subtract 2 from the right-hand side for each of the G times that we perform this operation: $F+V=E+2-2G$. G is called the genus of the polyhedron, the number of donut-like holes that it contains.

OK, enough abstract topology. Let's introduce the chemistry of the bonding. Can we make a closed polyhedron, with no dangling bonds, from sp^2-bonded carbon atoms? For sp^2 bonded carbon we need a new rule: each vertex has three edges emanating from it and each of these edges is shared between two vertices: $3V=2E$. This rule immediately requires that V be even: there are no closed carbon fullerenes with an odd number of atoms. Now graphene is made of hexagonal rings, so let's try to impose another condition: every ring of carbon atoms must have six edges. A polyhedron with purely hexagonal faces has 6 edges per face, each edge being shared by two faces: $2E=6F$. If we plug these two requirements ($E=\frac{3}{2}V$, $F=\frac{1}{3}E=\frac{1}{2}V$) into our rule $F+V=E+2-2G$, we obtain $G=1$. Our

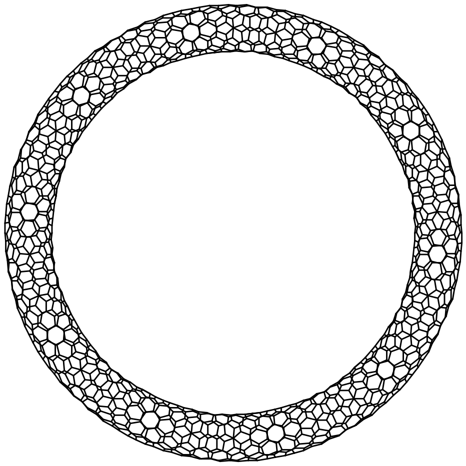

Figure 4: A ring

carbon structure with graphene-like bonding and hexagonal faces has a hole in it, like a donut! That is only a theorist's idealized picture of a nanotube (Figure 4). Usually, the theorist will think of the nanotube as perfectly straight, wrapping around onto itself at infinity. That's a nice idealization, but in real life, of course, no real nanotube is infinitely long (nor is it likely to wrap back onto itself seamlessly), so how does the end of a nanotube terminate without creating dangling bonds? One way is to cap the ends with metal particles or hydrogen atoms– we'll cover that possibility when we discuss open structures. Right now, we want to know how to make a closed polyhedral structure, with three-fold sp^2 bonding, but with no holes: $G = 0$.

Such a structure must contain fewer edges per face overall than our pure-hexagonal starting point. We can reduce the number of edges per face by using z-gons where $z < 6$ (for example, pentagons or squares). How many z-gons must we add to obtain a closed polyhedron with $G = 0$? A closed structure with N hexagons and M z-gons has $N + M$ faces, $\frac{6N+zM}{2}$ edges, and $\frac{6N+zM}{3}$ vertices. Plugging into $F + V = E + 2 - 2G$, we obtain a very simple answer: $(6 - z)M = 12(1 - G)$. The number of hexagons N is irrelevant, but for $G = 0$ the total depletion below purely hexagonal faces must be 12. Twelve pentagons suffice ($M = 12$, $z = 5$), as do 6 squares. The curvature from these z-gons bends the sp^2 sheet into a closed surface.

What z-gon does nature choose, and how are these z-gons arranged amongst the hexagons? The distortions in bond angles around a square embedded in a hexagonal network are about twice as large as the distortions surrounding a pentagon. Like any deviation from equilibrium, the energy cost is approximately quadratic in the distortion. Compared to two pentagons, the square then imposes a four times greater cost per atom across about half as many atoms. Therefore nature chooses pentagons. Similar arguments determine whether the pentagons are fused or separated by intervening hexagons. The two atoms shared by a pair of fused pentagons have about twice the local distortion in bond angle as have the atoms in separated pentagons. The fused pentagons contain 2 fewer atoms than a pair of separated pentagons, but they pay quadruple cost for the two shared atoms. Therefore nature prefers separated pentagons. Longer-range distortions then favor a uniform distribution of the twelve pentagons. *Note for the experts: These bond distortions are just a discrete analog to the continuum elasticity theory result that a spherical surface has minimal curvature energy.*

Therefore a carbon nanotube can pinch off into a close polyhedral structure by incorporating six pentagons into a roughly hemispherical cap on each end of the tube. One could also subtract off the belly of the tube, since it contains only hexagons, and connect the two endcaps into a roughly spherical closed cage, such as the C_{60} molecule, to which we return later.

Question: The transition metal dicalcogenides also form nanotubes. The fundamental structural subunit of these materials is a sheet with a triangular (not hexagonal) lattice. Derive the topological rules that determine the geometries of closed surfaces formed from sheets of transition metal dicalcogenides.

1.4 Curvature

The nanotube that we constructed above, with a straight belly composed entirely of hexagons plus two endcaps, each with six pentagons mixed into the hexagonal matrix, nicely illustrates the two mathematically distinct kinds of curvature that can be imposed on a graphene sheet. The cylindrical belly of the tube possesses mean curvature. This is the sort of curvature that one can impose on a sheet of paper without creating wrinkles or tears. Each of the pentagons acts as a point-like source of Gaussian curvature. Gaussian curvature is most easily thought of as the curvature of a sphere, the type of distortion that would wrinkle or tear a flat sheet of paper. Both types of curvature impose an energetic cost, since they weaken the overlap between the p_z orbitals of neighboring atoms.

Note to the experts: If one defines radii of curvature along the two principle axes passing through a given point on a surface, then the mean curvature at that point is the arithmetic mean of the inverses of the two radii of curvature, while the Gaussian curvature is the geometric mean of the inverses of these two radii. Since the radius of curvature of a cylinder is infinite along the axial direction, the Gaussian curvature of a cylinder is zero, while the mean curvature is finite.

1.5 Energetics

Now that we have covered the abstract geometrical requirements for a closed sp^2-bonded structure, let's consider the relative energies of various structures to get insights into why and how they form. In particular, we will examine why closed sp^2 bonded structures form in the first place. Later, when discussing kinetics, we will consider the distinction between ball-like structures such as C_{60} and long thin cylindrical structures such as carbon nanotubes.

Later chapters will give a more detailed description of fullerene synthesis; here we need know only that carbon clusters are produced in a high-temperature and low-density environment. The carbon source generally provides single carbon atoms or dimers that extend the growing structure, often in the midst of an unreactive buffer gas that helps encourage thermal equilibration. Tubes often grow while attached to a surface, such as that of a small metallic particle, whereas smaller ball-like fullerenes typically grow entirely in the gas phase.

If we want to use the relative energies of different structures to shed light on which ones are preferred during synthesis, we are restricted to situations where the system is near a thermal equilibrium. Only then does the system have time to explore the whole range of possible structures accessible to it; the lowest energy structure is then selected out as the system cools. As always in thermodynamics, one has to be careful about which degrees of freedom in the system are fast enough to become equilibrated and which ones are sufficiently slowed down (usually by large activation barriers or large phase spaces to explore) to prevent the system from accessing all possible configurations on the experimental timescales. Fullerenes typically grow very quickly in a highly transient environment. Therefore, if we want to keep things simple and consider all of the degrees of freedom to be thermalized, then we are restricted to considering only small clusters of atoms that have less configuration space to explore.

The smallest clusters of carbon atoms (those below about $N = 20$ atoms) do not form sp^2 bonds at all. Instead, they form linear chains. In this regime of very small sizes, where edges are very important, the decreased edge-to-interior ratio in one dimension favors chain-like structures (which have only two edge atoms at the exposed ends) over two-dimensional graphene-like structures. As the number of atoms in the cluster increases, the one-dimensional chains eventually became long enough that the reward for eliminating the two edge atoms outweighs the cost of bending, so the chains close into rings. However, one-dimensional structures make inefficient use of the strong carbon nuclear potential, since a linear structure has weaker overlap between the atomic potentials. In a double-bonded carbon chain, the binding energy for an interior atom is about 6 eV. The binding energy in a flat two-dimensional sp^2 sheet is larger, about 7.5 eV/atom. As the number of atoms in a cluster increases, the binding energies of the interior atoms begin to dominate;

the edge atoms and curvature become less important and the system transitions from one-dimensional chains with sp bonding to two-dimensional sheets with sp^2 bonds. *Note to experts: The transition from closed one-dimensional rings to closed two-dimensional sheets is perhaps best thought of as the favorable interior bonding energy in two dimensions overpowering the increased curvature energy which arises from the reduction in the radius of curvature from $R \sim N$ in one dimension to $R \sim \sqrt{N}$ in two dimensions.*

Are these sp^2-bonded sheets open like a bowl or closed like a ball? When an sp^2-bonded sheet is bent away from a perfectly flat geometry, the energy per atom goes up proportional to $1/R^2$, where R is the radius of curvature. *Note to experts: Why $1/R^2$ and not $1/R$? The curvature-induced change in the potential felt by the electrons is sensitive to the sign of R and hence proportional to $1/R$ (not $1/R^2$). The curvature introduces σ character into the π states and π character into the σ states. This hybridization is also sensitive to the sign of R and therefore is also proportional to $1/R$. Since the perturbation in the potential is odd, it only has a finite matrix element between perturbed and unperturbed portions of an electronic wavefunction. The two factors of $1/R$ then yield an energetic change proportional to $1/R^2$.* For a patch of graphene with N atoms, the characteristic linear dimension (which sets the size of the radius of curvature in a closed structure) is proportional to $\sqrt{N}$, so the bending energy per atom is proportional to $1/N$, and the total energy of bending is independent of the number of atoms. The energetic penalty for the edge atoms along the perimeter of an open graphene sheet goes up as $\sqrt{N}$. Since the energy cost of curvature in the closed structure is roughly constant, while the energetic cost of dangling bonds in the open structure goes up as $\sqrt{N}$, for large enough clusters a closed structure is lower in energy.

As we showed in the section on topology, every closed sp^2-bonded structgure has twelve pentagons and the most favorable such structures are those that separate out the twelve pentagons as evenly as possible and avoid having the edges of any two pentagons fused together (figure 5). In addition, since thermal equilibrium in the transient environment of fullerene synthesis can only be obtained for small structures, the best bet for being able to exploit thermodynamics to select out the most stable accessible structure is to choose the smallest structure that keeps the pentagons isolated from each other.

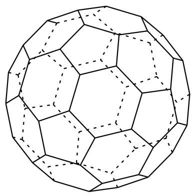

Figure 5: C_{60}

That structure is C_{60}. The next smallest isomer that also has isolated pentagons provides the second most common fullerene, C$_{70}$. C$_{70}$ consists of two C$_{60}$ caps with an extra row of hexagons in betweenlo. For larger-scale carbon polyhedra such as nanotubes, nanocones, or giant onion-like fullerenes, the system no longer has time to explore all possible configurations, so the types of structures produced are determined by a mixture of energetics and kinetics.

Question: As of yet, there are no known closed sheet-like structures formed from materials that prefer square lattices. Can you think of any candidate materials that might form such structures? Discuss the strengths and weakness of your candidates as regards the energetic and kinetic aspects of their putative syntheses.

1.6 Kinetics

In ever-larger sp^2-bonded carbon structures the curvature and/or edge atoms generally become less and less important and the energies of nearly all structures approach that of planar graphite. These larger structures do not have enough time to thermally explore all possible configurations, particularly since the strongly directional covalent bonding produces many metastable minima in the energy surface. Kinetics, meaning the nonequilibrium exploration of only a fraction of the possible structures, becomes more important. This dominance of kinetics over thermodynamics allows for a rich variety of large-scale structures.

The detailed microscopic mechanisms by which carbon nanostructures nucleate and grow remain largely mysterious, since growth is a fleeting and high-energy process that is difficult to characterize. However, the geometry of sp^2-bonded carbon imposes certain topological constraints that help us classify the possibilities. The first step towards creating a large-scale fullerene structure is to nucleate a small seed structure; the geometry of this seed then defines a growth zone, the part of the structure that incorporates the new carbon atoms as the structure grows. The geometry of the growth zone has a very strong influence on the shape of the final structure. These large-scale structures grow predominately through the addition of hexagonal rings, since the ring geometries in an active growth zone are reasonably well-thermalized and hexagonal rings are usually the lowest-energy sp^2-bonded rings.

We can consider three distinct geometrical possibilities for the seed, depending on how many pentagonal rings it contains: from one to five pentagons, from seven to eleven pentagons, or exactly zero, six, or twelve pentagons. A seed with one to five pentagons has less than half the Gaussian curvature necessary to wrap into a closed fullerene, so it defines a open expanding cone (Figure 6). These sp^2-bonded carbon cones have been made with all degrees of acuteness from one pentagon to five pentagons. Assuming that exclusively hexagons are added to the growing edge, the length of the cone's open edge expands as the square root of the number of atoms in the cone. Since the growth edge is ever-expanding, one expects that it eventually becomes difficult to maintain satisfactory growth conditions across this entire perimeter.

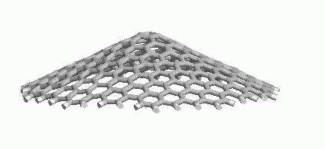
Figure 6: Cone

During growth, such a cone may occasionally add a pentagonal ring to the mostly hexagonal structure. Should the system accumulate seven or more pentagons, then the Gaussian curvature is strong enough to curl the seed structure from an outwards expanding cone into an inwards tapering cone (figure 7). As additional hexagons extend the structure, the open edge shrinks and eventually closes up upon itself, when it accumulates a total of twelve pentagons. The subtle interaction of bond angles and dangling bonds actually favors pentagons over hexagons once the growth edge tapers down into a sufficiently small opening. Eventually, the structure forms a large, somewhat lumpy closed fullerene. This sort of structure is favored in conditions that allow for the occasional creation of a pentagonal ring during growth.

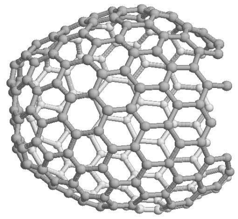
Figure 7: Taper

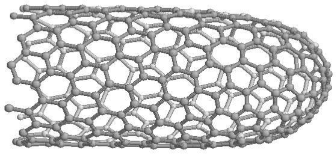
Figure 8: Tube closed on one end

What of the seed structures with exactly zero, six, or twelve pentagons? These structures are special: they have the ability to grow while maintaining a steady, unchanging growth zone. How? By extending the structure only in one dimension, the growth zone can retain a constant shape. A seed with zero pentagons is a sheet of graphene wrapped around into a belt with open edges at both ends (the only other option for zero pentagons is a flat sheet, which forms a simple graphene flake). Such a cylindrical seed could extend along its axis by adding hexagonal rings to the edges while maintaining an open edge of constant size. A seed with six pentagons forms a hemisphere. Adding hexagons to the open edge of such a seed will extend the edge to form a long thin cylinder (figure 8). Once a such cylindrical extension begins to form, it becomes very difficult to insert new hexagons into the hemispherical cap, since that would expand the cap and destroy the match in diameter between the cap and the cylindrical extension; (any such hexagons would quickly migrate into the cylindrical extension to re-match the diameters and thereby minimize strain). These zero and six pentagon seeds have one or two open edges; these edges could be either plugged by a metallic (or metal carbide) nanoparticle or left open to the environment. In either case, these highly reactive edge regions are likely to be the growth zones.

A seed with twelve pentagons is a closed fullerene with two hemispherical caps joined together (figure 9). Such a structure would act similarly to the closed hemispherical end of a six-pentagon seed. It is not yet clear experimentally if and when nanotubes grow from seeds with zero, six or twelve pentagons. However, the fundamental geometrical mechanisms favoring one-dimensional structures are identical in these three cases. These seeds can extend into a one-dimensional cylindrical shape whose growth zone maintains constant size and shape as the number of atoms increases. Since the growth edge retains its shape, the kinetics of growth remain constant and such a structure can grow very long.

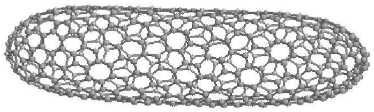

Figure 9: Tube closed on both ends

The energy of a long carbon nanotube is dominated by the $1/R^2$ curvature energy of the walls. Energetics plays a role in constraining the possible diameters: nanotubes with diameters smaller than about 0.7 nanometers suffer from reduced stability.

1.7 Other rings

Pentagons provide an efficient way to close up the structure and thereby cap dangling bonds. Heptagons, in contrast, open up the structure. Since expanding the edge of an open structure is normally energetically unfavorable, heptagons are less common in low-density synthesis conditions where dangling bond energy is more important.

Question: Describe why heptagons are energetically preferable to octagons as defects within a hexagonal graphene sheet.

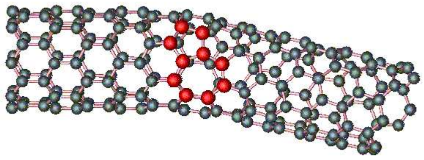

Figure 10: Junction

This expansion of the open edge can be avoided by pairing each heptagon with a pentagon. Just as one can add an arbitrary number of hexagons to a closed sp^2-bonded structure without disturbing the rule $F + V = E + 2 - 2G$, one can also add equal numbers of heptagons and pentagons. *Note to the experts: the Gaussian curvatures of the pentagon and heptagon cancel each other.* Such pentagon-heptagon pairs are observed: when the pentagon and heptagon are separated by intervening hexagons along the axis of a tube, the nanotube tapers (at the pentagon) and flares (at the heptagon). When the heptagon and pentagon are close together, the tube diameter does not change much, but the tube may bend abruptly (figure 10).

Question: Define the circumference of a nanotube as (n, m) in graphene lattice coordinates. How are the indices (n, m) changed when a pentagon/heptagon pair, is added to the structure of a growing tube? Treat only the special case where the pentagon and the heptagon share a bond in common.

1.8 Surfaces

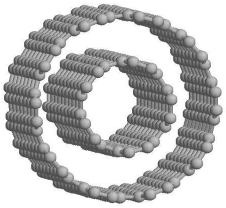

Figure 11: Two-walled tube

So far we have been considering only the energy of the σ and π bonding within a single graphene layer. However, these graphene layers also prefer to stack one atop another in graphite: Graphene sheets attract each other; pulling them apart and exposing free surfaces costs energy. This surface energy is very small, but can become important for large surfaces.

Sometimes the surface energy is important enough to open new kinetic pathways, wherein new atoms stick onto an existing sp^2-bonded surface and form another layer. The attractive interaction between two curved graphene layers is opposed by the $1/R^2$ curvature energy required to bend an outer incomplete sp^2-bonded patch into contact with the curved inner sheet. Therefore for sufficiently large R, an outer layer can form (figure 11). The crossover radius is very small, so nearly all fullerene structures would prefer to accrete additional outer layers, if the outermost layer is exposed to a source of new carbon atoms and synthesis conditions allow graphene-like patches to form on an exposed graphene surface. Multiwalled nanotubes and onion-like fullerenes result.

Nanotube synthesis can be catalyzed by metallic particles that plug the open end(s). Formation of outer layers is then suppressed (although an outer layer of amorphous carbon may form instead) and the tubes are predominately single-layered. However, the surface energy still plays a role: the growing tubes attract each other, aligning into bundles with the constituent tubes arranged into a roughly triangular lattice transverse to the bundle axis.

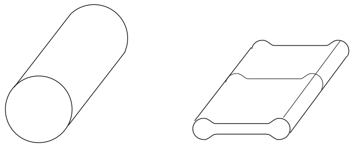

Figure 12: Flattened tube

The surface energy can also change the cross-section of an individual nanotube. Tubes with a large diameter can flatten into ribbons which take advantage of the attraction between opposing interior faces (figure 12). The energetic gain due to the intersheet attraction is proportional to the tube's diameter. The energetic cost of curvature is determined by the shape of the bulbs along either edge of the ribbon; this is essentially independent of the tube diameter. Therefore, the lowest-energy state of a large-enough diameter tube is flattened into a ribbon. Since the energetic curvature cost of any distortion from a circular cross-section is immediate while the gain in surface energy is short-ranged, there is a kinetic barrier against collapse. Experimentally, tubes with a particularly large internal radius can be flattened by a moderate uniaxial compression transverse to the tube axis. Single-walled tubes of diameter $\sim$1 nm are more stable when inflated than when collased.

Question: Write the surface energy per atom of a graphene sheet as ϵ. Write the mean curvature modulus (i.e. energy-length^2 per atom) of a graphene sheet as κ. The radius of the bulb on the edge of a flattened nanotube can be written as a function of a certain combination of ϵ and κ. What is this combination?

1.9 Holes ($G \neq 0$)

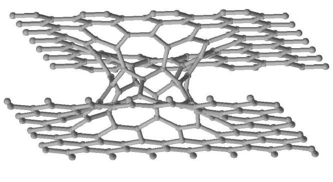

Figure 13: Wormhole

The topological rule $F + V = E + 2 + 2G$ implies that a structure with $G > 1$ must have an excess of heptagons over pentagons (figure 13). Since heptagons are disfavored in low-density conditions where dangling bond energies dominate, holey carbon structures should be prefered only in high-density synthesis conditions. The best such example is nanoporous carbon. Nanoporous carbons are formed by pyrolysis: at high temperatures the material decomposes into pure carbon plus various gaseous species that must escape from the still-forming disordered sp^2-bonded structure. These gases induce the formation of a disordered network of interconnected escape channels. Since the density of carbon in a pyrolyzing sample is much higher than that during a gas-phase fullerene synthesis, heptagons can form more readily. The resulting structure is complex, with a mixture of five-fold, six-fold and seven-fold rings, an unknown admixture of sp^3 bonds, and a very large number of holes. If we assume for simplicity that there are no sp^3-bonded carbon atoms, then the excess of heptagonal rings over pentagonal rings should be $12(G - 1)$ where G is the number of holes in the structure. The number of holes is equivalent to the number of times that the sp^2-bonded surface must be mathematically cut before one can contract the surface into a single giant closed fullerene ball (perhaps with some rather large rings).

1.10 Conclusion

Carbon's rich variety of two-dimensional structures arises not only from kinetics, but also because three-dimensional sp^3-bonded diamond-like structures are actually slightly less stable than graphite at zero pressure. The development of large, complex two-dimensional structures is not arrested by another transition in dimensionality, as happened for one-dimensional structures . In contrast to carbon, clusters of nearly all other elements are essentially always three-dimensional, with edge effects imposing at most a local surface reconstruction.

We end this section with the parable of the squirrel and the ant. A student asks a wise man whether a carbon nanotube is one dimensional, since it is long and thin, or two-dimensional, since it is composed of an sp^2 bonded sheet. The wise man responds, "Consider the squirrel and the ant. The squirrel, crawling on a telephone line, declares that the telephone line is a one-dimensional object, since the squirrel can scamper only back and forth along it. The ant, however, declares the telephone line to be two-dimensional, since it can happily crawl both along the length and around the circumference of the wire. So it is with the nanotube."

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