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Towards a fullerene-based nanotechnology:
The (10,10) tube

by
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A THESIS SUBMITTED
IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE

Doctor of Philosophy

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Abstract

Towards a fullerene-based nanotechnology:

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Andreas Theß

While fullerenes form in yields exceeding 30% by mass when a laser generated pure carbon vapor is allowed to condense under annealing conditions, more than 70% of all vaporized carbon assembles in the form of single-wall fullerene nanotubes (SWNTs) in the presence of certain transition metal SWNT catalysts. Due to the high carbon to metal ratio in the vapor will the early stages of condensation, even in the presence of a SWNT catalyst, be characterized by an abundance of all-carbon fullerene-precursors. Metal atoms will then condense onto these clusters as condensation proceeds, and SWNTs are nucleated from fullerene-precursors interacting with a metal vapor as an off-shoot of the road leading to C_{60}-fullerene. Electron nano-diffraction performed on crystalline strands of aligned SWNTs demonstrates that samples are dominated by tubes of "armchair" geometry, while X-ray diffraction shows a narrow diameter distribution, centered around 1.36 nm. In conclusion, the particular armchair tube matching the observed diameter, labeled the (10,10) tube, is the most prominent individual tube in the investigated samples. The astonishing efficiency with which armchair tubes form suggests that carbon clusters tend to anneal towards armchair geometries even in early stages of condensation, eventually rearranging into bowl-shaped fullerene-precursors with their open edge energy reduced by formation of triply-bonded pairs of 2-coordinated carbon atoms. In a pure carbon environment, such fullerene-precursors are predetermined to close into C_{60}-fullerene. In the presence of a SWNT catalyst however, metal atoms diffusing (scooting) along the growing edges of fullerene-precursors prevent their closure, forcing them to
grow into tubelets with an open, growing armchair edge instead. The optimum diameter of such tubelets results from competition between strain energy in their cylinders (favoring tubelets of large diameters) and open edge energy (favoring tubelets of small diameters). At annealing temperatures, tubelets will initially widen their diameters as they add more carbon to reduce strain. Beyond a certain size however, clusters will finally have too many atoms to rearrange on the relevant time scale. At this time, their diameters get kinetically frozen due to shear size, and a diameter distribution centered around the (10,10) tube diameter is locked in place.
Acknowledgment

The work presented in the following would not have been possible without the support of many friends. They have provided an atmosphere that made science a truly enjoyable and stimulating experience. This environment is what allowed and encouraged me to grow as a scientist.

Far beyond providing the opportunities that make truly exciting research possible, over the years Dr. Richard Smalley's example and guidance developed in me a deep appreciation for the challenge the unknown poses. Dr. Dieter Heymann and Dr. Lon Wilson have been a constant source of valuable feedback and ideas throughout my time at Rice. Dr. Felipe Chibante was the first member of the Smalley group to take me under his wings on an everyday basis. His admirable talent to both get things done and at the same time make every member of the team feel valued has left a lasting impression with me. Following this period, Dr. Mike Alford, Dr. Ting Guo, and Mr. Michael Diener proved to be valuable mentors, passing their vast experimental expertise. Dr. Ting Guo is also the person who taught me how to let the basketball roll off your fingertips, especially when shooting the three-pointer. The time I spent with Mr. Pavel Nikolaev, Dr. Andrew Rinzler, and Dr. Hongjie Dai resulted in an extraordinarily fruitful period, giving rise to much of the results presented here. For many years, Dr. Daniel Colbert provided me with new insights during countless discussions. In the hectic we inevitably created, the affable atmosphere provided by Mrs. Mary Widner often came to the rescue.

Outside the academic environment, I would like to thank Dr. Frank Roschangar, who has been a special friend now for almost a decade. His cheerful character has been a constant source of inspiration. Finally, my special thanks go to my parents. Their love and encouragement have provided the needed support for my ventures throughout my life.
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Introduction

In 1985 experiments were conducted in labs at Rice University designed to better understand the formation mechanism of small carbon molecules. When allowing a carbon vapor to condense, it was found that under certain conditions a cluster containing 60 carbon atoms was markedly more abundant than other clusters in the same size-range. In order to explain the special stability of the C\textsubscript{60} molecule, it was proposed to have a highly symmetric spherical structure with 12 pentagonal faces and 20 hexagonal faces arranged to form a hollow cage build completely from carbon. For the first time, the specialty of the C\textsubscript{60} molecule was recognized. It was called Buckminsterfullerene in honor of the american architect and philosopher Buckminster Fuller, whose geodesic domes, constructed of interlinked hexagons and pentagons, follow the same architectural principal. Soon it was realized that C\textsubscript{60} is only the most prominent member of a whole family of hollow carbon cages, dubbed the "fullerenes", of which C\textsubscript{70}, C\textsubscript{76}, C\textsubscript{78}, and C\textsubscript{84} are other important members. They all contain 12 pentagons, introducing curvature into the carbon network to allow closure of the cage, and a varying number of hexagons.

While at the time C\textsubscript{60} was discovered relatively small clusters were readily studied, only later became it feasible to study high mass clusters with many hundreds of atoms. It was found that the distribution of even numbered clusters so characteristic of the fullerenes actually can extend out to beyond 600 carbon atoms. Choosing the right conditions results in an almost exclusive conversion of carbon vapor into fullerenes, including a distribution of "giant fullerenes". It became clear that fullerenes like C\textsubscript{60} and C\textsubscript{70} are only part of a whole new class of finite carbon structures based on graphene carbon sheets.

In 1991 tubular structures built from several concentric cylindrical layers of carbon hexagons with capped ends were discovered on the negative electrode of an arc discharge
apparatus similar to those used for production of fullerene containing soot. Individual layers of these multi-wall carbon nanotubes (MWNTs) can be thought of as elongated fullerenes, a graphene sheet curved into a cylinder sealed off at each end by a hemi-fullerene dome. Shortly thereafter, tubes having walls of single layer graphene sheets were synthesized by arc discharge, single-wall carbon nanotubes (SWNTs).

Since then, further study has greatly extended our knowledge about the properties of fullerene based structures and applications are beginning to emerge. Early on it was shown that doping the interstitial sites of the C₆₀ lattice with Alkali metals results in a superconducting phase. Potential biological applications include enzyme inhibition, antiviral activity, DNA cleavage, photodynamic therapy, and electron transfer. Much excitement has been stimulated by reports of C₆₀ blocking the active site of HIV-1 protease, pointing towards possible medical usage of fullerenes. The potential use of fullerenes containing radioactive metal isotopes trapped inside the cage in radiotherapy is under investigation. Alternatively, contrast agents for magnetic resonance imaging could be based on endohedral fullerenes containing elements with high nuclear magnetic moment. In either case the closed carbon cage around the metal would prevent undesired interaction inside the body. Carbon fibers of unsurpassed strength based on defect free SWNTs are of high interest as building material. SWNTs might also impact the field of composite materials since contact between fibers and matrix can be maximized for tubes with single layer walls. Field-emission of electrons from a linear chain of carbon atoms attached to the end of an open MWNT has been observed. Such an atomic wire has potential to be an excellent coherent point source of monochromatic electron beams. By applying a voltage pulse rather than a continuous voltage, it may be possible to extract single electrons from such a structure. Arrays of aligned MWNTs have been demonstrated to give field-emission current densities of more than 100 milliampere per square centimeter. Due to their very high aspect ratio and small diameter, MWNTs used as probe tips in atomic force microscopy (AFM) have been found to be superior in imaging deep and narrow surface morphologies. Yet, unlike conventional AFM tips, they
are mechanically flexible and not easily damaged upon crashing into the sample surface. Due to the electrical conductivity of nanotubes, the same probe ending in a single tube can be used for scanning tunneling microscopy. Fabrication of probes ending in an individual SWNT of roughly one nanometer diameter can be expected to do wonders in terms of consistently achieving high resolution in AFM. Probes ending in one SWNT of known helicity and diameter would be the first probes ever where the location of every atom on the tip is exactly known. Could this be the ultimate probe? The chemistry at the caps sealing off SWNTs can be expected to parallel the chemistry of fullerenes. How about the realization of chemical sensors and scanning catalytic probes by chemically derivatizing the dome closed end of a nanotube? Another application bridging between nanoscopic and macroscopic world is the use of carbon nanotubes as miniaturized electrodes. Of special interest are such structures where the electrochemistry is restricted to proceed only at the very tips. The successful synthesis of boron nitride nanotubes suggests that this could be achieved by coating the sides of tubes with an insulating layer of boron nitride.

In the remainder of this text, work will be presented that greatly enhances our understanding of the principals governing the self-assembly of fullerene based structures, the final goal being the rationale synthesis of nanoscopic objects defined on the atomic scale. The progress reported here already proves valuable for the development of tools and imaging or measuring devices connecting the nanoscopic to the macroscopic world. This fullerene based nanotechnology is part of a more general trend in technology towards miniaturization of established techniques as well as the devise of new, nanoscale solutions, which will ultimately allow us to observe, understand, and manipulate on a molecular level.
Synthesis of fullerenes

The arc and its limitations

In the experiments that lead to the discovery of $C_{60}$, graphite was vaporized by intense pulsed laser irradiation. Expansion of the resulting plasma was contained by a high density stream of room temperature helium. During this expansion, small carbon species grew larger as they collided to yield a distribution of carbon clusters. Upon leaving the vaporization chamber, clusters were cooled by supersonic expansion of the inert gas, subsequently ionized by an excimer laser, and detected in a time of flight mass spectrometer. When the helium pressure was high enough, fullerenes were produced. Later the yield of soluble fullerenes under these conditions was determined by high performance liquid chromatography to be 0.01% by weight \(^{20}\). Unfortunately, since only microscopic amounts of fullerenes could be produced by this technique, a thorough characterization of $C_{60}$ and higher fullerenes like $C_{70}$ and $C_{84}$ remained elusive for many years after their discovery.

The field of fullerenes really took off after Huffman and Krätschmer led the way to bulk production of $C_{60}$ and other fullerenes in 1990 with their resistive heating technique \(^{21,22}\). In their apparatus, a conically sharpened graphite rod was forced into contact with an opposite larger graphite electrode. Through this arrangement, a current was passed. As the resistance is greatest at the narrow point of contact between the electrodes, most of the power is dissipated in ohmic heating in this confined region. In time, the tip of the sharpened electrode is evaporated and the area of contact between the 2 electrodes increases. Fortunately, a fraction of the evaporated carbon forms a layer of amorphous carbon between both electrodes so that this zone remains the zone of highest resistance. Thus, the bulk of the power still dissipates in this small zone even as evaporation progresses. The vaporized carbon deposits as a condensate ("soot") on the walls of the
evaporation chamber and contains $C_{60}$ and higher fullerenes. Yields of soluble fullerenes exceeding 20% were obtained. Like in the original laser evaporation experiment, the confining inert gas atmosphere was at room temperature. However, compared to the rapid temperature drop that species experience in the expanding plasma generated by a laser, species get cooled much more slowly as they diffuse out of the evaporation zone, which is a constant heat source. The resulting soft temperature profile allows clusters to anneal much more efficiently until they find the optimum fullerene geometry, whereas rapid cooling does not allow a cluster to sample geometry space, and defects get frozen in.

The limiting factor for this method becomes apparent when one tries to produce more fullerenes simply by scaling up the apparatus: Only for small rods does the amorphous layer between the electrodes stay sufficiently resistive, for bigger rods (6mm diameter or bigger), soon the entire rod begins to glow. As temperatures above 3000°C are required to evaporate graphite at a significant rate, the energy loss due to blackbody emission from the rod becomes enormous. Also, the rod evaporates fastest at its center and eventually breaks, interrupting the electric circuit.

Today the most common way of evaporating graphite in such a reactor is to pass a current through 2 carbon electrodes while a small gap is maintained between them, generating a confined plasma, or arc, between the electrodes $^{24, 25}$. Here the bulk of the power is not dissipated in ohmic heating, but rather in the arc, and thus only the small gap region is heated. Because the 2 rods are close to each other compared to their diameters, most of the radiative power of the plasma is absorbed by the electrode surfaces, making this method very power efficient. The main problem of the arc method is unveiled by Table 1, which shows typical yields as a function of rod diameter. Even though the arc method allows one to use carbon electrodes of larger diameter than the resistive heating technique used by Huffman and Krätschmer, generally the yield goes down as the electrode diameter is increased. The technique does not scale up very well.
<table>
<thead>
<tr>
<th>Rod diameter</th>
<th>0.125 inch</th>
<th>0.25 inch</th>
<th>0.5 inch</th>
<th>1 inch</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fullerene yield</td>
<td>25%</td>
<td>15%</td>
<td>8%</td>
<td>3%</td>
</tr>
</tbody>
</table>

Table 1: Fullerene yield in the arc as a function of rod diameter

It has been mentioned earlier that the temperature profile of the inert gas atmosphere is critical for the clustering process and thus for a high yield. Considering this, in principal the highest yields should be obtained when the evaporation of carbon and the clustering conditions are controlled separately. In an attempt to implement this principal, the machine shown in Figure 1 was built \(^{36}\). The main feature are 2 carbon rod electrodes approaching each other at a 30° angle that reach into the heated zone of a 1200°C tube furnace through which a stream of inert gas flows. By sweeping the carbon vapor quickly out of the arc into the tube furnace, the clustering should then take place under conditions set by the furnace rather than the arc. Surprisingly, despite optimization of parameters like gas velocity, oven temperature, and arcing current, the yield was extremely poor, below 3%. In a design with straight on electrodes, a yield of 15% is easily achieved with 6 mm diameter rods. In summary, arc synthesis of fullerenes leaves several questions unanswered:

1) Even though the temperature profile provided by the arc is apparently important for the fullerene yield, it is not clear at what temperature fullerenes actually form.
2) How long does it take a growing cluster to anneal into C\(_{60}\)?
3) What is the physical process causing the yield to drop when attempting to scale up the arc synthesis of fullerenes, and is the adverse effect of the oblique electrode orientation related to this problem?

Answers to the first two questions are relatively straightforward to find and will be presented in the next section “Laser oven and annealing”. The scale up problem will turn out to result from a feature of the arc not yet considered. The section on solar generation of fullerenes will solve the mystery.
Laser oven and annealing

With these problems in mind, the combined laser-oven-setup shown in Figure 2, similar in design to a previous version \(^2^5\), was set up to produce fullerenes by laser vaporizing carbon under a heated inert gas atmosphere. Such a setup allows far greater control over growth conditions than the arc since the various parameters involved can be controlled individually. A graphite target was supported by graphite poles in a one inch diameter quartz tube, which in turn was positioned inside a high temperature tube furnace (Lindberg, 12 inches long), with a maximum temperature of 1200°C. Before runs the quartz tube was evacuated to 10 mtorr and then backfilled with an inert gas atmosphere (argon or helium). Flow of the inert gas through the quartz tube was controlled by a mass flow controller on the inlet side (MKS 1159) in combination with a needle valve at the outlet side. Graphite was evaporated by directing a pulsed, focused laser beam (Continuum DCR-16S at 532 nm, 10 Hz) down the quartz tube onto the face of the target.
Vaporized carbon then clustered at a temperature set by the oven. The laser beam was scanned across the target surface by a computer controlled, motor driven total reflector (two 850-1B motors, 45° at 532 nm) to maintain a smooth, uniform face for vaporization. The condensate ("soot") was entrained in the stream of inert gas and swept from the high temperature zone to deposit on a water cooled collector mounted downstream from the target just outside the oven. The fullerene yield in this setup was then optimized by varying selected parameters. A compilation of the conditions used in several runs, and the corresponding fullerene yield can be found in the Appendix "Parameters in fullerene production". These experiments lead to a new level of understanding of the factors important to the formation of fullerenes.

![Diagram of laser oven setup](image)

Figure 2: Laser-oven-setup

The laser flux was carefully adjusted by changing the focus of the laser beam. Together with the gas type and gas pressure, the laser flux will determine the feedstock-density during fullerene growth. The highest yields were obtained at a loose laser focus producing a relatively low carbon density. Apparently clusters cannot incorporate pentagons fast enough to close by the time they are 60 atoms big when the feedstock-density is too high. Annealing simply cannot keep up with cluster growth. At lower feedstock-density,
fullerene-precursors can anneal before they have to incorporate new feedstock. This shows that in the formation of fullerenes by laser vaporization, annealing is the yield limiting factor. A tight laser focus producing a high carbon feedstock-density actually favors the formation of multi-wall tubes \(^{20}\). Due to frequent collisions, often a second graphene sheet will nucleate on a growing carbon cluster. This second graphene sheet is likely to grow conforming to the first sheet, and eventually its growing edge catches up with the open edge of the initial layer. Interaction of the dangling bonds on these 2 sheets (called "lip-lip" interaction) will then stabilize their open edges and prevent closure of the cluster, forcing it to grow into a tube instead.

The fullerene yield was found to increase with increasing temperature in the range between room temperature and 1200°C (the maximum oven temperature). Higher temperatures were no tried. From this behavior it is concluded that annealing is optimized at temperatures equal to or higher than 1200°C. (Compare these findings with the first question left unanswered in the section "arc generation and its limitations".)

It is instructive to compare these results with the original laser vaporization experiments where the plume expanded into roomtemperature helium rather than a heated inert gas atmosphere, giving clusters only a limited time to anneal \(^1\): As mentioned before, the yield of soluble fullerenes under these conditions was later determined by HPLC to be only 0.01% \(^{20}\). However, much of the other carbon also formed fullerenes, much larger ones which are not soluble. These giant fullerenes \(^3\) form since clusters grow very large before they finally include enough pentagons to close, indicating that much of their growth occurs at temperatures too low to anneal efficiently. When expanding into 500 torr of roomtemperature helium, it takes the plume on the order of one microsecond to cool below 1100°C (see Appendix "Plume expansion"). Thus, even when expanding into roomtemperature helium, good annealing conditions are provided during the first microsecond of growth. Apparently, clusters do not anneal into closed structures during the first microsecond and the formation of fullerenes like \(C_{60}\) takes several microseconds
or longer, so that the later stages of their growth are affected by the temperature of the inert gas atmosphere inside the oven. (Compare these findings with the second question left unanswered in the section "arc generation and its limitations").

Fullerenes were produced both under helium and argon atmospheres. The effects of the inert gas are twofold: The expansion of the plume is restricted by the inert gas. Argon will restrict more efficiently and thus result in a higher feedstock-density during the clustering process. The inert gas also cools the expanding plume and thus has great influence on annealing. Since the collision between a C₂ or C₃ radical and argon will result in a higher momentum transfer than a collision with helium, argon will cool the plasma faster (both helium and argon have the same heat capacity). In the laser-oven-setup, the heated atmosphere helps to maintain good annealing conditions over an extended period. The pulsed vaporization of carbon though will result in a rapidly dropping feedstock-density during plume expansion. Accordingly, the fullerene yield was found to be higher under argon atmosphere due to its ability to more efficiently restrict plume expansion. The higher cooling efficiency of argon does not pose a problem in a heated atmosphere. Contrary to that, the feedstock-density is less of a concern in an arc generator since the arc is a constant source of fresh carbon. Here too rapid cooling of clusters by the room temperature atmosphere has to be prevented. Indeed, the yield in an arc generator is typically higher under helium, which cools less efficiently.

Under argon the fullerene yield is maximized at a pressure of 500 torr. At higher pressures, the yield drops off slowly, while at lower pressures the drop in yield is more pronounced. This dependence of the yield on the inert gas pressure may partly result from the small diameter of the quartz tubes used: A pressure of 500 torr or above may be necessary to efficiently prevent material contained in the expanding plume from hitting the walls of the one inch quartz tube. The flow has not been found to strongly affect the fullerene yield. However, a sufficiently high gas velocity is necessary to collect material efficiently on the water cooled collector. At slow gas velocities, a larger fraction of the
soot deposits inside the oven on the walls of the quartz tube and does not reach the collector.

The fullerene content of the soots deposited on the water cooled collector was extracted with toluene. Extracts had the wine-red color characteristic of high-yield fullerene soots. Extraction was followed by detection of the fullerene content by high pressure liquid chromatography (Waters 510 pump, 996 photodiode array) on a reversed phase column (Waters Nova-pak C_{18}, 4\mu m particle size, 60Å pore size, 3.9mm × 300mm column dimension) with toluene/methanol (50:50 at 2 ml/min.) as the eluent. Fullerene yields were estimated by comparison with calibrated standards at 306 nm. With the photodiode array the various fullerenes could be identified by their characteristic UV/vis spectra, allowing to estimate the relative abundance of different fullerenes.

The conditions under which the highest yield of extractable fullerenes were obtained can be summarized as follows:
- Temperature of the inert gas atmosphere: 1200°C
- Gas type: argon
- Gas pressure: 500 torr
- Gas flow (gas velocity): 50 sccm (1.7 cm/s)
- Laser repetition rate: 10 Hertz
- Laser pulse energy: 300 mJ
- Laser fluence: 14 mJ/mm²

Under these conditions, 68% of all material vaporized by the laser deposited on the water cooled collector. Depending on definition, the fullerene yield was 44% (weight of fullerenes extracted from the collected soot divided by the weight of the collected soot) or 30% (weight of fullerenes extracted from the collected soot divided by the weight loss of the target). The relative abundance C_{60}:C_{70}:higher fullerenes was roughly 40:30:20, as can be seen in the chromatogram in Figure 3.
Figure 3: Chromatogram of laser-oven fullerenes
Solar generation and photochemical death

The laser-oven-setup produces fullerenes in very high yield. Unfortunately though, while laser vaporization in an oven has advantages, it is not suited to large-scale production. Laser photons are simply too expensive. Thus, it is now time to return to the scale up problem of the arc method and the stunning drop in yield observed for electrodes at an oblique angle.

Compared with other designs, there is one principal aspect that is different about the oblique arc: ultraviolet radiation. Because of the oblique angle, the intense UV radiation from the central portion of the plasma is now fully exposed to the condensing carbon clusters as they flow downstream in the quartz tube. Considering the evidence for photoinduced polymerization of fullerenes 28, 29, 30, 31, 32 it is conceivable that photochemical destruction of fullerenes may be the principal factor controlling the yield in arc generators.

While the newly formed fullerenes are moving away from the region around the arc, they are exposed to intense light flux. Absorption of light efficiently produces an excited triplet state \( (T_1) \), which lives for a few microseconds \(^{33}\), before the molecule relaxes back down to the ground electronic state, \( S_0 \).

\[
C_{60}(S_0) + h\nu \rightarrow C_{60}^*(T_1)
\]

Fullerenes such as \( C_{60} \) absorb at all wavelengths below about 700 nm, but the absorption cross-section in the ultraviolet below 350 nm is 10 to 100 times stronger than in the visible. Ultraviolet light is therefore particularly effective, even though rapid internal conversion and intersystem crossing will produce the \( T_1 \) state regardless of photon energy.
While the fullerene is in this $T_1$ state, it is an open-shell species, far more susceptible to reaction with other carbon species, $C_x$, than it was in the closed-shell $S_0$ state. The result of most such reactions will be to produce a nonvaporizable, insoluble product.

$$C_{60}^*(T_1) + C_x \rightarrow \text{insoluble carbon}$$

Since the rate of bimolecular photochemistry increases linearly with the photon flux and $C_x$ concentration, it is a particularly significant problem within a few rod diameters of the electrode tips in the arc method. As the rod diameter is increased, this photochemically dangerous region becomes larger in direct proportion to the rod size, but the rate of migration of the fullerenes through this zone remains roughly constant. Therefore, the yield of fullerenes which make it through this zone without reacting will decrease linearly with rod diameter. This agrees with the observed dependence of the fullerene yield in arc generators on electrode diameter. (Compare these findings with the third question left unanswered in the section "arc generation and its limitations".)

Most arc generators feature directly opposed electrodes separated by only a small gap. Due to this small gap, vaporization proceeds fast, and the concentration of reactive species $C_x$ is high. Fortunately though, due to the small gap, most of the ultraviolet light is blocked by the electrodes themselves, limiting the rate at which fullerenes are photoexcited. However, if the angle between the rods is made oblique, the ultraviolet light flux is significantly increased. Assuming that the gap between electrodes is still kept small, now both the rate of vaporization and thus the concentration of $C_x$, and the rate at which fullerenes are photoexcited, are high. The result is the dramatic reduction in yield observed for the oblique arc.
The chief problem for large scale production of fullerenes therefore appears to be how one can prevent photochemical destruction of the fullerenes emerging from a vaporization region that is always hot and - more problematically - always BRIGHT.

In order to minimize the photochemistry, it appears necessary to transport the carbon vapor into a relatively dark zone before the fullerenes have begun to form. Furthermore, it will be helpful to allow the carbon vapor to expand, so that the concentration of reactive \( C_x \) species is so low that it is very unlikely that a fullerene excited to the \( T_1 \) state will suffer a reactive collision within its lifetime. This expansion will happen naturally as the carbon vapor is drawn away from the vaporization source by the inert carrier gas, if somehow the condensation process can be postponed. So how does one keep carbon from clustering?

Ironically, the answer to how to minimize cluster photochemistry may involve more light. Imagine simply overwhelming the clustering by photolysis (and concomitant thermolysis) induced by intense sunlight. Figure 4 shows a conceptual sketch of a fullerene generator which utilizes focused sunlight both to vaporize a carbon target (in zone 1) and to maintain the carbon as an essentially atomic vapor (through zone 2), until it passes into the shadow where clustering is finally permitted to occur (zone 3). The key feature of this scheme is zone 2, the bleaching zone. In this zone, close to the radiating source of carbon vapor, the heat provided by an intense flux of sunlight simply does not allow carbon to cluster. Instead, clustering is postponed until the level of dangerous radiation has dropped sufficiently in zone 3.
As an initial demonstration that fullerenes can in fact be produced by direct sunlight, the apparatus shown in Figure 5 was assembled. Sunlight was collected by the parabolic mirror (Melles Griot, electroformed nickel with rhodium finish, 35.6 cm outer diameter, 6 cm focal length) and focused onto the tip of a 0.4 mm diameter graphite rod (Poco Graphite AXM-5Q). As shown in the figure, this rod was mounted inside a 58 mm inner diameter, 2 mm wall, 30 cm long Pyrex tube and arranged such that it could be translated along the optic axis of the paraboloid. To minimize the extent of conductive heat loss, and to help anneal the carbon clusters as they grew from the vapor, the graphite rod was enclosed by a helical tungsten preheater (8 turns on a 3 mm diameter cylinder, 10 mm length, 0.25 mm diameter tungsten wire) mounted 3 mm below the tip of the target rod. The system was evacuated to less than 30 mtorr and degassed with the preheater for several hours to remove absorbed gasses from the graphite rod, purged, and then refilled with 50 torr of argon and sealed off. The apparatus was then mounted on the yoke of an 8 inch equatorial telescope mount (Celestron Pacific) and adjusted so that the sunlight was focused directly on the tip of the graphite target. With careful alignment of the equatorial axis to the earth's rotation, the motorized telescope mount was easily able to track the sun for several hours without need for further adjustment.
The solar fullerene generation apparatus was operated for 3 hours (11 a.m. to 2 p.m.) on a day when the direct solar flux at the site (at 1400 m elevation in the Franklin Mountains near El Paso, Texas) was measured to be 800 to 900 W/m². Over the 3 hour experiment, 5 mg of carbon was evaporated from the target. During operation, the central axis of the evaporator made an angle of 10-25° from vertical while tracking the sun. As a result, the argon gas heated by the tungsten preheater was efficiently carried up over the solar irradiated carbon tip by convection, and the condensing carbon vapor was quickly swept out of the intense sunlight and cooled in the upper regions of the Pyrex tube. The condensate subsequently deposited on the upper walls of the Pyrex tube. Extraction of the deposited soot with toluene gave a wine-red solution very similar to extract obtained from soots produced by either the arc method or the laser oven method. Figure 6 shows the
HPLC analysis of the soluble fraction, demonstrating that its fullerene content was predominantly $C_{60}$ and $C_{70}$.

This result is impressive as a first demonstration of the potential use of solar energy for the production of fullerenes. Large scale solar production of fullerenes has subsequently been implemented by others $^{34, 35}$. It remains to be shown that focused sunlight can be used effectively to prevent condensation of the carbon vapor in a bleaching zone until it passes into a dark cluster formation and annealing zone.
Figure 6: Chromatogram of solar fullerenes
Metallofullerenes

Fullerene-precursors and metals of low electronegativity

Shortly after the discovery of C\textsubscript{60}, evidence was obtained that the space inside the hollow fullerene carbon network could hold a variety of species bound to the inside of the cage, an entrapped La atom being the first example \cite{36}. Alternatively, the fullerene cage itself can be modified, for example by exchanging a carbon atom for a boron atom \cite{37}. Finally, it is possible to attach species to the outside of a fullerene, as is realized in the epoxide C\textsubscript{60}O \cite{38}. This ability to modify the bare fullerenes allows one to fine-tune their properties.

Small amounts of fullerenes holding a metal inside, called metallofullerenes, were initially produced in the laser oven simply by adding a small amount of certain metals to the graphite target \cite{37}. Subsequently, metallofullerenes were also produced in the arc \cite{39}. Experimentally it is found that only metals of low electronegativity form metallofullerenes. Not surprisingly then, La\textsubscript{12}C\textsubscript{82} was shown by electron spin resonance \cite{40}, X-ray photoelectron spectroscopy \cite{41}, and ultraviolet photoelectron spectroscopy \cite{42} to be more accurately described as La\textsuperscript{3+}\textsubscript{12}C\textsubscript{82}\textsuperscript{3-}. Metallofullerenes can thus be thought of as charge transfer complexes. Which metals can be entrapped by a fullerene cage can actually be predicted solely on the basis of the electronegativity of the metal in question \cite{43}. While the arc proved capable of providing large amounts of soot though, the fraction of fullerenes that actually contained one or several metal atoms was only modest, at best.

Would the optimized laser-oven-setup at hand produce metallofullerenes in reasonable quantities and higher yields? Assuming that conditions optimum for fullerene production will also be optimum or close to optimum for the production of metallofullerenes, and in view of the high fullerene yields obtained, the answer should be yes! At the basis of this assumption stands the consideration that since in the laser generated plume the metal will
only start to condense at much lower temperatures than carbon, the presence of the metal will initially have little effect on the formation of fullerene precursors. The formation of metallofullerenes then is the result of vastly abundant fullerene-precursors interacting with a metal vapor. Based on the charge transfer character of metallofullerenes, this interaction is likely mainly ionic, with a metal bound to the side of the graphene sheet (rather than the metal interacting in a more covalent fashion with the dangling bonds at the edge of the graphene sheet). It is straightforward to see how such a metal atom would get enclosed inside a fullerene cage as the graphene sheet continues to include pentagons and eventually closes. The graphene sheet wraps around the metal atom. This model is supported by the notion that interaction of a metal atom with the $\pi$-electron cloud of the graphene sheet will be more favorable on the inside of a curved graphene bowl than on its outside, where the $p$-orbitals, which dominate the $\pi$-electron cloud, are pointing away from each other. The picture is complete after also considering that a metal atom interacting with the bowl might actually aid in curving the graphene sheet.

The presented picture suggests that the laser-oven-setup had already been optimized for production of metallofullerenes when the setup was optimized for fullerene production. Accordingly, metallofullerene containing soots were produced under the conditions listed towards the end of the section "laser oven and annealing". Graphite targets were doped with either 0.5% by mole Lanthanum or 0.5% by mole Yttrium.

To answer the question what fraction of fullerenes actually contained (a) metal atom(s) inside, the volatile fraction of soots was sublimed onto water cooled copper disks. X-ray fluorescence measurements on these sublimed films revealed the amount of metal present. Measurements were performed on a wavelength dispersive Rigaku spectrometer with a LiF (200) crystal, the X-ray source operating at 50 kV and a current of 50 mA. Observed was the $K_\alpha$ line of Yttrium. Subsequently these films were dissolved in toluene and their fullerene content determined by HPLC. Typically, 7% of the fullerenes sublimed out of the soot were metallofullerenes. For comparison, Bandow et al. have reported a
tenfold increase in the abundance of metallofullerenes in their soots produced by the carbon arc method when using LaC$_2$-enriched composite rods rather than La$_2$O$_3$ containing composite rods $^{44}$. With this improved technique, they estimate that the Lanthanofullerenes they produced constitute about 3% by weight of the extract from the soot.

To determine the yield of fullerenes in the soots, and thus the level of metallofullerenes, soots were extracted with toluene, followed by HPLC analysis of the extracts. Typically, soots contained fullerenes at a level of 15% by weight, 7% of which should be metallofullerenes according to the previous paragraph (assuming that both toluene extraction of the soot and sublimation of soots transfer comparable amounts of fullerenes out of the soot). Thus, metallofullerenes account for roughly 1% by weight of the metallofullerene soots produced in the laser-oven-setup. This value compares very favorably with the estimate by Bethune et al. that metallofullerenes typically "constitute less than a few weight percent of the extractable species (or $\leq 10^{-3}$ of the soot) (italics added)" $^{45}$.

The result that metallofullerenes are synthesized in high yield under conditions that would produce fullerenes in high yield in the absence of metal confirms the mechanistic basis underlying the entrapment of a metal atom by a fullerene cage presented above: Metallofullerenes form as an off-shoot of the road leading to C$_{60}$ due to metal condensing onto fullerene-precursors during the clustering process.
Single-wall Fullerene Nanotubes

Fullerene-precursors and metals of high electronegativity

It has now been shown that both in the laser oven and in the arc the addition of certain metals of low electronegativity leads to the formation of metallofullerenes. The question then arises how metals of higher electronegativity might affect the clustering process. In the arc it has been demonstrated that the addition of certain such metals with an electronegativity similar to carbon leads to the formation of SWNTs $^5$. $^6$. It is straightforward to extend this same approach to the laser oven. Initially these experiments were performed in a laser-oven-setup identical to the setup described in the chapter “Laser oven and annealing”. During the course of the experiments, this setup evolved into the apparatus described later in the section “The big tube apparatus”.

Targets were uniformly mixed composite rods of either half inch or one inch diameter. The preparation of a one inch diameter target with a metal concentration of 1% cobalt plus 1% nickel involved the following steps: 4.847 g Co(NO$_3$)$_2$·6H$_2$O and 4.843 g Ni(NO$_3$)$_2$·6H$_2$O (both Aldrich, 99.999%) were dissolved in 100 ml water. To this solution, 10 g of graphite powder (Carbone of America, ultra “F” purity) were added. The resulting slurry was then heated while stirring so that the metal salts eventually dried onto the graphite particles. After the powder had been dried overnight at 130°C, it was ground in a mortar, followed by the addition of 14.286 g of carbon cement (Dylon). After thorough mixing, the paste so produced was placed in a one inch diameter stainless steel mold. The mold was placed in a hydraulic press equipped with heating plates (Carver model C) and baked at 130°C for 4-5 hours under constant pressure. Finally, the baked rod was removed from the mold and cured under an atmosphere of flowing argon in a programmable tube furnace (Lindberg 54233) at temperatures up to 1200°C.
Soots produced by laser vaporizing such targets doped with a small amount of transition metal deposited either on the water cooled copper collector or directly on the quartz tube just outside the furnace. Samples to assess the content of such deposits were prepared by sonicating one hour in methanol, and examined using a JEOL 2010 transmission electron microscope (TEM) with beam energy 100 keV. Figure 7 shows a typical TEM image. Not surprisingly, the material does contain SWNTs in the form of tangled fibers 10 to 20 nm in diameter and many micrometers long. Depending on the sample quality, ropes as long as 100 μm have been observed. In addition to nanotubes also amorphous carbon, multi-wall capsules (onions), and metal particles enclosed in carbon can be seen. Remarkably, no TEM image ever revealed MWNTs in these samples. In case the nanotube yield was high enough, deposits could be removed as a cohesive sheet of material (named the “felt” after its appearance).

Like metallofullerenes, SWNTs are synthesized under conditions that produce fullerenes in high yield if no metal catalyst is added. Thus, similar to metallofullerenes, the formation of SWNTs also appears to be the result of fullerene-precursors interacting with a metal vapor. Compared to metals leading to the formation of metallofullerenes, metals leading to the formation of SWNTs are of higher electronegativity, similar to the electronegativity of carbon. Such metals, unable to form charge transfer complexes, are more likely to engage in covalent interaction, that is, interact with the dangling bonds after diffusion leads them to the edge of the graphene sheet. What a difference it makes!

While multi-wall carbon nanotubes come with random numbers of concentric shells and thus are not a well defined material, this variable has been eliminated in the production of single-wall carbon nanotubes. This important step towards a well defined material will be beneficial both for the characterization of carbon nanotubes as well as progress towards the use of nanotubes in practical materials.
Figure 7: SWNTs in the TEM at low magnification
Super-Duper SWNTs

When a solid is laser vaporized, ablation of loosely connected target flakes, splashing of molten target material, deep target heating that leads to explosion of bubbles, and condensation in the high density plume often lead to the presence of micron and submicron particulates in the plasma. However, exposing such a plume to a second laser pulse can often drastically reduce the level of particulates. This dual laser vaporization is in principle also applicable to the laser vaporization of carbon, and thus to the generation of SWNTs in the laser-oven-setup.

To implement this dual laser approach, the initial green laser pulse was followed after a short delay with a second laser pulse to provide additional heat, probably to both the plume and the face of the target. In the most optimistic scenario, the following factors all might result in an increased SWNT yield:

a) Exposing the plume to a second laser pulse will ensure that condensation starts from what resembles more closely an atomic vapor due to laser induced plume heating. Energy from the second laser could couple into the plume via either of the following two mechanisms: (1) Light could be absorbed by micron-sized particles in the plume. (2) Light could also be absorbed by small radicals in the plume. See Appendix "Laser induced plume heating" for an estimate of how much energy this mechanism could deposit in the plume.

b) Metal and carbon will mix more homogeneously as a secondary effect of the more complete vaporization.

c) Plumes generated via dual laser vaporization will cool slower since they contain more material. (This assumes that the molar heat capacity of the material contained in the plume is roughly independent of laser conditions. Specifically, it is assumed that the degree of ionization in the plume is roughly independent of laser conditions, for example.) While the annealing of tubes is likely just as facile at 1200°C as...
the annealing of fullerenes, higher temperatures will favor the disassembly of large feedstock by the catalyst.

d) The feedstock-density in a plume generated by the dual laser technique will be higher, since expansion of the plume is still limited by the speed of sound. Such a higher feedstock-density can increase the SWNT yield in the following ways: (1) The formation of fullerenes is limited by the ability of carbon itself to anneal into its most favored structure. A high carbon density during the clustering process will result in the formation of a lot of imperfect fullerenes, imperfect onions, and structures kept open by lip-lip interactions. These imperfect clusters formed at high densities, featuring open edges with dangling bonds, will be easier to digest as feedstock than perfectly closed structures, which would result from extensive annealing at low carbon densities. Due to the action of the metal catalyst however, tubes will be able to assemble incoming carbon into a defectfree network even under high feedstock-densities. (2) Furthermore, a larger fraction of all carbon can be eaten before the density has dropped so low that growth effectively comes to a halt.

The result of the double laser vaporization can be seen in Figure 8. The image clearly shows that the optimistic scenario just presented must contain some elements of truth: Up to 90% of all the carbon vaporized appears to condense in the form of single-wall carbon nanotubes, giving the deposit the appearance of a "nano brillo pad".51.
Figure 8: Super-Duper material in the SEM
Parameters

During the course of both single laser and dual laser experiments, several factors have been elucidated to be important in rope growth:

A series of metal catalysts was evaluated for yield of SWNTs under single laser vaporization conditions with the oven set to 1200°C. Yield here refers to the fraction of vaporized carbon that condensed in the form of SWNTs. Estimating SWNT yields from TEM images is semi-quantitative at best, since the density of ropes is much lower than the density of other components of the felt, like amorphous carbon for example. Thus, emphasis in interpretation of these data should be put on comparison between the various catalysts, not on exact figures for the yield. Table 2 lists the metals used as catalyst and the corresponding tube yield. As can be seen, the yield varies greatly, despite all metals having similar electronegativity. While the formation of metallofullerenes can be predicted based on electronegativity, this simple approach is only of limited use to predict the effectiveness of a certain metal as a catalyst for SWNT formation. Of the metals tried, nickel was found to give the highest tube yield. Seraphin compiled a similar survey of various catalysts in the arc \(^5\). Some of the yield trends seem to be in qualitative agreement. Although comparison of the data is difficult due to the different experimental setups, the discrepancy in the case of iron is striking however: While in the laser oven the yield was exceedingly low with iron as catalyst, a high density of SWNTs is found in the deposit inside the arc chamber with iron as catalyst. Iijima, more in agreement with findings from the laser-oven-setup, found that iron does not catalyze the formation of SWNTs unless methane, which probably serves as a feedstock, is present inside the arc chamber \(^5\).
Table 2: SWNT yield for various catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Concentration (% by atom)</th>
<th>SWNT yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>0.6</td>
<td>5</td>
</tr>
<tr>
<td>Co</td>
<td>1.0</td>
<td>0.5</td>
</tr>
<tr>
<td>Pt</td>
<td>0.2</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Fe</td>
<td>1.2</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Mo</td>
<td>1.0</td>
<td>none</td>
</tr>
<tr>
<td>Cu</td>
<td>0.6</td>
<td>none</td>
</tr>
<tr>
<td>Nb</td>
<td>0.6</td>
<td>none</td>
</tr>
<tr>
<td>Y</td>
<td>0.5</td>
<td>none</td>
</tr>
</tbody>
</table>

In the arc it has been found that binary metal mixtures can significantly enhance SWNT yields \(^{53}\). Similarly, mixing metals that produce SWNTs individually increased the yield of SWNTs in the laser oven technique, sometimes dramatically. Table 3 lists the binary metal catalysts used and the corresponding tube yield under single laser vaporization conditions. Of the combinations tried, a mixture of 50% cobalt and 50% nickel gave the highest nanotube yield.

Table 3: SWNT yield for various binary catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Concentration (% by mole)</th>
<th>SWNT yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni/Co</td>
<td>0.6/0.6</td>
<td>50</td>
</tr>
<tr>
<td>Ni/Co</td>
<td>0.85/0.35</td>
<td>50</td>
</tr>
<tr>
<td>Co/Pt</td>
<td>0.6/0.2</td>
<td>50</td>
</tr>
<tr>
<td>Ni/Pt</td>
<td>0.6/0.2</td>
<td>20</td>
</tr>
<tr>
<td>Ni/Fe</td>
<td>0.6/0.6</td>
<td>30</td>
</tr>
<tr>
<td>Ni/Y</td>
<td>0.6/0.6</td>
<td>20</td>
</tr>
<tr>
<td>Co/Cu</td>
<td>0.6/0.5</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Co/Fe</td>
<td>0.6/0.6</td>
<td>&lt;0.1</td>
</tr>
</tbody>
</table>
While the model that individual metal atoms interact with the growing edge of a tubelet can explain how fullerene-precursors are kept open and forced to grow into tubes, this assumption cannot explain the yield enhancing effect of bimetallic mixtures. Only if actual catalytic particles are involved in some phase of the growth process, containing a mixture of the two metals, rather than metal atoms interacting individually with the open edge, can the positive effect of bimetallic mixtures be explained.

This suggestion that soon after nucleation actual particles act as catalyst might explain why a platinum catalyst never grows long tubes: The observation that only short tubes form shows that Pt is able to nucleate tubes, but not able to sustain growth. If in the later stages of condensation SWNTs grow from actual particles, the high melting point of Pt (1772°C) relative to other catalysts might be at the root of this problem: As the plume cools to the temperature of the oven, Pt particles get effectively frozen. With particles deprived of the fluctuability necessary to ensure a high carbon diffusivity through their interior, SWNT growth comes to a rather abrupt halt.

How do binary mixtures actually do the trick? It seems most likely that the 2 metals part of a binary mixture are at their best at different growth stages. To illustrate this point, consider a Pt/Co catalyst. As just noted, Pt is able to nucleate tube growth, but is not able to sustain growth. Co on the other hand is clearly able to sustain growth. The combination of a metal able to nucleate growth with a metal able to sustain growth might just make a great SWNT catalyst. An increased diffusivity of carbon through binary catalyst particles due to an increased void space in a mixture might also contribute to the enhanced SWNT yield observed for binary catalysts. Segregation of the two components, leaving the surface of catalytic particles highly able to dismantle and digest feedstock, while concentrating the metal of higher carbon diffusivity at their core also might offer an explanation.
Variation of the catalyst concentration showed that a metal loading between 1% and 2% is optimum. At lower catalyst concentration, the SWNT yield rises dramatically over a very small concentration range as the optimum metal concentration is approached. Beyond the optimum concentration, the SWNT yield goes slowly back down. Under dual laser vaporization conditions using the optimum catalyst concentration, as much as 90% of all carbon vaporized condenses in the form of single-wall carbon nanotubes, a much higher fraction than obtained by the arc discharge method. Table 4 lists the SWNT yield under single laser vaporization conditions as a function of Ni/Co loading.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Concentration (% by mole)</th>
<th>SWNT yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni/Co</td>
<td>0.05/0.05</td>
<td>1</td>
</tr>
<tr>
<td>Ni/Co</td>
<td>0.10/0.10</td>
<td>20</td>
</tr>
<tr>
<td>Ni/Co</td>
<td>0.15/0.15</td>
<td>40</td>
</tr>
<tr>
<td>Ni/Co</td>
<td>0.30/0.30</td>
<td>50</td>
</tr>
<tr>
<td>Ni/Co</td>
<td>0.60/0.60</td>
<td>50</td>
</tr>
<tr>
<td>Ni/Co</td>
<td>1.2/1.2</td>
<td>50</td>
</tr>
<tr>
<td>Ni/Co</td>
<td>2.4/2.4</td>
<td>50</td>
</tr>
<tr>
<td>Ni/Co</td>
<td>5.0/5.0</td>
<td>30</td>
</tr>
</tbody>
</table>

Table 4: SWNT yield for various Ni/Co loadings

The maximum yield achieved in a dual laser experiment at 1100°C is 65%. Yields up 90% were obtained in dual laser experiments at 1200°C. However, raising the temperature further to 1250°C or 1300°C did not increase the maximum obtained yield noticeably. Likely annealing conditions do not improve further at temperatures beyond 1200°C. The similar dependence of both nanotube yield and fullerene yield on temperature (the fullerene yield also was substantially lower at 1100°C) could either mean that fewer tubes are nucleated as fewer fullerene-precursors are formed at lower
temperature (since SWNTs grow as an offspring of fullerene formation), or that fullerenes are an important feedstock, less of which is available at 1100°C.

In general, the laser powers will affect the temperature of the plume and the carbon density during the clustering process. During optimization of the single laser vaporization process it was determined that up to a certain point the yield of SWNTs increases with tighter laser focus. This might be related to the fact that at a tighter laser focus, more energy of the laser pulse will be absorbed by material in the plume itself. This might improve the homogeneity of the vapor before clustering starts and also improve annealing. Laser vaporization is a self-limiting process in terms of useful laser power: if the laser light is too intense, the later part of the pulse will be reflected by the laser generated plasma, and less material is vaporized. Exceeding this limit resulted in a definite drop in SWNT yield. In addition to this limiting effect of the laser generated plasma, the mechanical strength of targets can further lower the useful laser power: Above a certain threshold, target material is blown off the face of the target as dust rather than vaporized. Exceeding this limit also resulted in a drop in yield. For dual laser vaporization, it appeared that the yields were highest when the green laser approached either the plasma or the dust limit. Yields were less sensitive to the IR flux. In general, the SWNT yield optimized at higher laser fluxes than did the fullerene yield. This agrees with what has been said about the possible effects of a high feedstock-density under dual laser conditions.

It was found that the SWNT yield was highest when the delay between both lasers was short. At the same time, the mass vaporized by a pair of lasers fired in close succession more than totaled the mass evaporated by both lasers when they were run individually. A short delay might either optimize interaction of the second laser with material contained in the plume, or might be required for dual laser vaporization to generate bigger/denser plumes than can be achieved with a single laser. Such big/dense plumes could not have been achieved by simply firing a single laser with more power per pulse, since once a
certain amount of energy is deposited, the plasma created by the laser becomes dense enough to reflect incoming light, wasting the later part of the laser pulse. The high evaporation rate under dual laser conditions seems to be due to a cooperative effect between the two lasers: When the first laser irradiates the target, the number of monolayers that can be heated to above the evaporation temperature of carbon during the duration of the laser pulse is limited by thermal conduction of heat into the depth of the target. When the second laser irradiates the surface of the target a short while later however, energy deposited by the first laser in deeper layers that did not evaporate during the first laser shot is still available so that during the duration of the second laser pulse more monolayers reach a temperature above the evaporation temperature of carbon. Thus, preheating of the target by the first laser pulse allows the second laser pulse to actually evaporate more mass than the first laser pulse. A limit to how short the delay can be made is given by the lifetime of the plasma created by the first laser. If the second laser is fired too early, it will get blocked by the plasma left from the first laser and vaporize little or no material at all.

Repetition rates of 2, 5, 10, 15, and 30 Hertz were tried. It is found that going from 2 Hz to 5 Hz and then to 10 Hz the SWNT yield increases. This indicates that material vaporized in one shot interacts with material vaporized in either previous or subsequent shots. Apparently different plumes interact. Going from 10 Hz to 15 Hz or even to 30 Hz does not affect the SWNT yield significantly.

The suggested plume-plume interaction is confirmed by the fact that the volume that the plume expands into needs to be restricted. In such a restricted volume it is possible for different plumes to affect each other. One possible explanation for this observation might be that fullerenes formed in previous shots are important as feedstock. Restricting the volume that the plume expands into effectively increases the fullerene concentration during the formation and growth of tubes. Alternatively, the need for a small volume in front of the target might not stem from plume-plume interaction, but from the fact that
such a small volume could reach a significantly higher temperature. In this scenario, the temperature of the oven (1200°C) would not be the optimum growth temperature. However, since raising the oven temperature from 1200°C to 1250°C or even to 1300°C does not further improve the yield, there seems to be no explanation why such a locally higher temperature should improve the yield.

**Advanced laser-oven-setup**

Optimization of the parameters presented in the last section eventually lead to a later version of the laser-oven-setup more elaborate than the initial setup. The basic principal is simple: Material vaporized by the lasers initially expands upstream into the restricted volume of a narrow diameter quartz tube. The condensate then gets carried downstream by flowing gas into a large diameter quartz tube to allow collection of large amounts of felt material (see Figure 9).

A 2" diamete: quartz tube, supported in the front and back by 2 water cooled aluminum endpieces (the front and rear flange), is mounted inside a tube furnace. Centered on the axis of this tube is a shorter 1" diameter quartz tube extending from the front flange to the hot center of the oven, where it is supported by a graphite baffle. While the front flange includes a quartz window at Brewster's angle to allow laser beams to enter the chamber, the rear flange supports a rod extending into the furnace used to position a cylindrical graphite target doped with a small amount of transition metal catalyst so as to extend 1 cm into the opening of the inner quartz tube. The target can be centered in the smaller quartz tube via 4 setscrews integrated into the rear flange, causing the rod to pivot in its O-ring seat.
For operation, the chamber is pumped to a pressure < 10 mtorr, leak checked, and then backfilled with inert gas. Gas is metered in via a mass flow controller connected to the front flange and leaves the chamber through a control valve connected to the end flange. After entering the chamber, gas flows initially through the inner quartz tube. Its velocity drops as it passes the target to enter the larger quartz tube. The pressure inside the chamber is monitored by a capacitance pressure gauge. A controller provided with information about the pressure by the pressure gauge and in charge of the mass flow controller is programmed with a pressure setpoint and adjusts the control valve accordingly to keep the pressure at the programmed setpoint.
2 Nd-YAG lasers optimized to lase at 30 Hz are externally controlled via a Camac crate containing 2 timing generators capable of generating voltage pulses with μs precision (microsecond timers) and 1 timing generator capable of generating voltage pulses with ns precision (nanosecond timer). One microsecond timer recycles continuously and triggers the second microsecond timer at a frequency of 30 Hz. Any time the second microsecond timer is triggered, it generates a pulse sequence to fire both lasers and trigger the nanosecond pulser. It also provides a pulse used to synchronize an oscilloscope. The nanosecond pulser q-switches both lasers, allowing the delay between both laser pulses to be controlled to ±1 ns. In addition, the Camac crate houses 1 Camac controller receiving instructions from a PC via Gpib interface. A Labview program running on the PC initializes the Camac crate, determines the required number of pulses to be generated, writes the information necessary to specify all pulses in the appropriate registers on the timing generators, and finally starts the first timing generator. Once the first timing generator has been started, no further action by the PC is required.

To ensure reproducible beam profiles, both lasers are run at full flashlamp energy and the delay between firing of the flashlamps and q-switching is held constant, optimized for maximum pulse energy. A concave/convex lens pair in the path of the green laser allows to adjust the area on the target in which the laser ablates. The maximum spot size is determined by the power of the green laser. A concave/convex lens pair in the path of the infrared (IR) laser allows the IR spot size to match the green spot size. This way, both lasers have the same diameter on the target. The IR power is reduced via an attenuator so that the power can be changed without changing the spot size or beam profile. If necessary, the green power can also be reduced via an attenuator.

For the green laser it is necessary to match the polarization of the IR light emerging from the amplifier with the orientation of the harmonic generation crystal by rotating the half wave plate in front of the second harmonic generation housing. The green light leaving
the harmonic generation housing is not horizontally polarized, as is required for maximum transmission of green light by the Brewster's angle window attached to the front flange of the oven. The polarization of the green laser light emerging from the harmonic generation housing is thus rotated to horizontal via a half wave quartz plate. After being combined using a beamsplitter, the green and IR beam spatially overlap and thus copropagate. To facilitate alignment of all optical components, a Helium-Neon laser (HeNe) beam also copropagates with the green and IR beams. The green and HeNe laser beams are reflected of 2 mirrors each before being combined at the beamsplitter to provide the necessary degrees of freedom for accurate overlap with the IR beam. (In the case of the green laser, this beamsteering is accomplished simply via the second harmonic isolation optics integrated into the laser.) A quartz prism of sufficient quality to eliminate thermal lensing directs the beams onto the target, where they arrive separated by a short delay controlled by the nanosecond timer.

After passing the prism, a small fraction of the laser beams can be picked off by sliding a quartz wedge into the beam path, while the transmitted part of the beams is then dumped in a beam stop mounted on the same carrier supporting the quartz wedge. Part of the reflection is fed into a CCD camera after the intensity of the beams is further reduced by neutral density filters. A PC equipped with a framegrabber card allows to analyze the profile of each beam and is also used to monitor the spatial overlap of green and IR laser. In order to ensure that images taken by the CCD camera faithfully represent the conditions at the target, the distance between quartz wedge and target is identical to the distance between quartz wedge and CCD camera. Another fraction of the beams picked off by the quartz wedge is directed onto a photodiode under 9 V reverse bias to measure the time delay between green and IR pulse. Pulses are displayed on a digital storage oscilloscope triggered by the synchronization pulse available from the second microsecond timer.
The oven is located close to the lasers. In the far field, laser beam profiles are smooth, but laser beams approximate a gaussian. Due to the wide wings of such a profile, a lot of energy is distributed in the outer parts of the beam, but only over a small fraction of the beam cross-section is the light flux intense enough to vaporize carbon. Contrary to that, close to the lasers the available energy can be used more efficiently since here the beam profiles are somewhat flatter with most power concentrated in an area of sufficient light flux to vaporize carbon.

To ensure uniform vaporization of the target, the prism directing the beams onto the target is scanned under computer control with the use of 2 actuators. A Quickbasic program allows to define the area to be scanned using the keyboard. Subsequently, a scanning pattern is calculated and the turning points defining the pattern are retrieved from memory for each complete scan.

Table 5 specifies some of the components mentioned in the previous sections:

<table>
<thead>
<tr>
<th>component</th>
<th>make/model</th>
</tr>
</thead>
<tbody>
<tr>
<td>oven</td>
<td>Lindberg/Blue M HTF55322A</td>
</tr>
<tr>
<td>vacuum gauge measurement and control system</td>
<td>MKS type 146</td>
</tr>
<tr>
<td>pressure gauge</td>
<td>MKS Baratron 122AA</td>
</tr>
<tr>
<td>mass flow controller</td>
<td>MKS 179</td>
</tr>
<tr>
<td>control valve</td>
<td>MKS 248A</td>
</tr>
<tr>
<td>Nd-YAG laser</td>
<td>Spectra Physics GCR-250</td>
</tr>
<tr>
<td>Camac crate</td>
<td>Kinetic Systems 1502 Crate</td>
</tr>
<tr>
<td>Camac controller</td>
<td>Kinetic Systems 3988 Gpib Crate Controller</td>
</tr>
<tr>
<td>microsecond timer</td>
<td>Kinetic Systems 3655 timing generator</td>
</tr>
<tr>
<td>nanosecond timer</td>
<td>LeCroy 4222 pulse and delay generator</td>
</tr>
<tr>
<td>attenuator</td>
<td>Newport high power variable attenuator 935-10</td>
</tr>
<tr>
<td>CCD camera</td>
<td>COHU 4812-7000/0000 solid state camera</td>
</tr>
<tr>
<td>beam analyzer</td>
<td>Spiricon LBA-300PC laser beam analyzer</td>
</tr>
<tr>
<td>actuator</td>
<td>Newport 850B-1</td>
</tr>
<tr>
<td>motion controller</td>
<td>Newport motion master 2000</td>
</tr>
</tbody>
</table>

Table 5: Components of an advanced laser-oven-setup
Following is an example of specific conditions under which Super-Duper material was obtained:

Temperature of the inert gas atmosphere: 1200°C

Gas type: argon

Gas pressure: 500 torr

Gas flow (gas velocity) in the inner quartz tube: 100 sccm (3.4 cm/s)

Metal loading: 1% by mole Co + 1% by mole Ni prepared from Nitrates

Green laser pulse: 460 mJ in a 6.35 mm diameter spot (8% clip off limit)

Infrared laser pulse: 560 mJ in a 6.37 mm diameter spot (8% clip off limit)

Laser repetition rate: 30 Hz

Time delay: 42 ns

Vaporization rate: 230 mg / hour
Morphology of SWNTs

While it has been reasoned that SWNTs form as an off-shoot from the road leading to \( C_{60} \), a detailed mechanism is still missing. To develop such a detailed mechanism though, it is first necessary to characterize the products found in the felt more thoroughly.

Ropes

TEM inspection of the nanotube material at high magnification shows that individual tubes align, running together in van der Waals contact over most of their length (see Figure 10). These highway structures, also called ropes, contain up to between 100 and 500 SWNTs. Except for occasional branching, ropes maintain a constant diameter over their entire length. Only in runs of very low yield can individual tubes be found. Interestingly, the SWNTs produced in the laser oven are very clean. Typical arc produced SWNTs are covered with a thick layer of amorphous carbon, limiting their usefulness. Much less such coating is seen with tubes produced here. This may at least partly be related to the high yields obtained, since less carbon is freely available to coat the sides, and also because the bundling results in much less surface area to coat. The ends of ropes can rarely be found. Remarkably though, in the lucky instance that the end of a rope is seen, usually all SWNTs running in parallel terminate within a few nanometers of each other, the ends of all tubes apparently perfectly closed with hemispherical endcaps. Sometime a rope comes into the field of view, curves around as it goes through the focal plane of the microscope, and then leaves into the direction it came from. In this case one looks at a cross-section of the rope in the focal plane (see Figure 11). Both from images normal to the rope axis and from cross-sectional views it becomes apparent that SWNTs self-organize and crystallize into a two-dimensional (2-D) lattice.
Figure 10: Ropes contain hundreds of aligned SWNTs
Figure 11: Cross-section of a rope showing uniformity of tube diameters
Tube diameter

The fact that tubes within a rope crystallize necessarily means that the diameter distribution of tubes has to be narrow. Closer examination of TEM cross-sectional views confirms this critical point: The tube diameters are highly uniform. The observed organization of nanotubes with a narrow diameter distribution into a 2-D lattice within the ropes triggered the search for X-ray diffraction (XRD) intensity that would confirm the existence of this 2-D lattice. To eliminate the possible interference of small fullerene crystals present in the felt, several tens of milligrams of felt were heated under $10^{-6}$ torr vacuum to 1000°C for 30 minutes, causing the fullerenes to sublime out of the felt.

XRD was performed at 300 K in the flat plate geometry on a 1 cm by 1 cm piece (5 mg) of the heat treated felt, which readily adhered to an etched Si(111) wafer moistened with ethyl alcohol (see Figure 12). The diffractometer was a sealed Cu tube (wavelength $\lambda = 1.54 \text{ Å}$) operating at 1 kW, with a flat graphite(002) monochromator, a fixed sample angle at grazing incidence, and a linear detector (radius 25 cm) that allowed parallel accumulation of 4096 channels covering 120° in 2θ. Since the flat plate diffractometer had no provision for rotating the sample during data collection, several flat plate profiles collected at different incident angles were compared. Consistent relative intensities for the various runs showed that ropes had no preferred orientation in the sample.

The low-Q region is dominated by small-angle scattering ($Q = 4\pi\sin\theta/\lambda$). A strong discrete peak occurs near $Q = 0.44 \text{ Å}^{-1}$ ($2\theta \sim 6^\circ$), as do four weaker peaks (up to $Q = 1.8 \text{ Å}^{-1}$) that are consistent with a 2-D triangular lattice. A small, sharp peak occurs at 1.85 Å$^{-1}$, which is very near the graphite(002) position; the XRD-profiles of MWNTs are dominated by this reflection$^{54, 55}$. Peaks at 3.06 and 3.54 Å$^{-1}$ were identified with (111) and (200) reflections of Co-Ni. The integrated intensity of these Co-Ni peaks is related to the amount in which they are present in the heat treated felt. The upper limit for their
concentration is 1.2% by mole, the concentration in the target used to produce the felt. The integrated intensity of "graphite(002)" is at least an order of magnitude lower, indicating that less than 0.1% by mole of all carbon is present as MWNTs or as capsules or possibly as adventitious graphite from the target. Notably absent is the graphite (100) expected at $Q = 2.95 \text{ Å}^{-1}$, which is observed in MWNTs with a line shape perturbed by the curvature of the graphene sheets. Evidently, the more severe curvature of the smaller SWNTs broadens the (hk0) reflections to such an extent that they are no longer detectable. The sizable background in Figure 12 comprises air scattering (dominant below 2 Å$^{-1}$), incoherent (Compton) scattering (independent of Q), and diffuse scattering from amorphous carbon. The important observation is that - apart from signatures of trace Co, Ni, and possibly MWNTs, carbon capsules, or graphite - the XRD-profile is dominated by Bragg peaks that are entirely consistent with the TEM images.
Figure 12: XRD-profile of SWNT material total counts versus $Q = 4\pi \sin \theta / \lambda$. 
The XRD data was analyzed in detail by first fitting the entire profile to a sequence of discrete reflections of arbitrary line shape plus a polynomial background. The fitted background was subtracted from the raw data (shown in Figure 13, trace a). The initial attempt to index this difference profile on a triangular lattice led to major discrepancies in several positions, which could not be satisfactorily accounted for even by considering a lower symmetry - namely, a centered rectangular lattice with $b/a \neq \sqrt{3}$. The sixfold symmetry could be broken for a number of reasons: (1) several closely spaced, but distinct tube diameters could be present; (2) curvature of the ropes; or (3) frustration of the close packed lattice if the symmetry of a dominant SWNT is incompatible with sixfold rotation.

The problem was solved by realizing that due to the particular nature of the SWNT form factor, in combination with the broad peaks [$\Delta(2\theta) \sim 0.5^\circ$] arising from the finite diameter of the ropes, experimentally observed intensities in general cannot be expected to coincide with the "infinite crystal" Bragg positions:
Figure 13: Fit to the XRD-profile
Data-fitted background (curve a) compared with a model profile (curve b) that assumes a 2-D triangular lattice of uniformly charged cylinders, \(a = 1.695\) nm, and circle radius \(R = 0.69\) nm. Vertical tick marks on curve b are the calculated Bragg positions. Curve c shows how the square of the Bessel function form factor \(J_3(QR)\) distorts the broadened reflections in position and shape, in addition to modulating the intensities.
The charge density averaged over an ensemble of randomly oriented C\textsubscript{60} molecules is that of a spherical shell of charge. The Fourier transform of such a uniform shell of radius \( R' \) is \( j_0(QR') \), where \( j_0 \) is the zero-order spherical Bessel function, and might serve as an ad-hoc form factor \(^{56, 57, 58}\). Potentially, \( j_0 \) might alter the intensity, position, and shape of reflections from a C\textsubscript{60} crystal. However, in solid C\textsubscript{60}, the crystalline coherence length is large, so the XRD peaks are extremely sharp, and in practice \( j_0 \) is expected to modulate only the observed intensities. This simple model was successfully used to explain the at first surprising absence of (200) reflections in the XRD-profile of crystalline face centered cubic C\textsubscript{60}, in which the C\textsubscript{60} molecule is freely rotating at room temperature \(^{56}\). By analogy, assuming no azimuthal correlations between SWNTs within a rope, the SWNT form factor is well approximated by the spherical Bessel function \( J_0(QR) \) (shown in Figure 13, trace c), where \( R \) is the SWNT radius. However, there is one important difference. The finite diameter of rope crystals produces broad peaks \( \left[ \Delta(2\theta) \sim 0.5^\circ \right] \). Moreover, the oscillations in \( J_0 \) are spaced roughly twice as closely as in \( j_0 \), and \( R \) is about twice \( R' \), such that the diffraction widths observed in SWNT ropes are an appreciable fraction of the width of the lobes in \( J_0 \). Thus, not only does \( J_0 \) modulate the intensities of the peaks (as does \( j_0 \) for a C\textsubscript{60} crystal), but the positions and shapes of the peaks are modulated as well. Accordingly, calculated maxima (shown in Figure 13, trace b, for a peak broadening of 0.5\(^\circ\)) coincide with the "infinite crystal" Bragg positions (Figure 13, vertical tick marks in trace b) only for reflections that happen to lie near peaks in \( J_0 \). As a result, the lattice constant and tube diameter must be optimized simultaneously, and the calculated profile is very sensitive to both \( a \) and \( R \); deviations in either parameter lead to discrepancies in relative intensities, widths, and positions. The best fit was obtained with a lattice constant \( a = 1.68 \) nm and a tube radius \( R = 0.68 \) nm. The uncertainties for \( a \) and \( R \) are estimated as \( \pm 2\% \) and \( \pm 1.5\% \), respectively. The van der Waals gap (\( a - 2R \)) is 0.315 nm; this gap size, about the same as in solid C\textsubscript{60} \(^{58}\), is 0.03 nm less than the turbostratic limit for graphite, and is consistent with a calculation for a lattice of somewhat smaller nanotubes \(^{59}\). Apparently, the interaction between nanotubes 1.36 nm in diameter is not sufficiently strong to distort their cylindrical shape, as was predicted to occur for tube
diameters exceeding 1.5 to 2.0 nm\cite{60}. The observed peak width yields a coherence length of 10 nm, which is consistent with the diameters of the ropes observed in the TEM images. In summary, the observation of well defined 2-D lattice reflections confirms that the SWNT diameter is highly uniform.

After realizing just how narrow the diameter distribution is, the question had to be asked: How in the world is it possible that all the tubes born in the chaos of a carbon plasma end up having such similar diameters? It has been suggested that polyyne rings serve as nuclei for growth of single-wall fullerene nanotubes\cite{61}. Clearly, this model cannot explain the observed uniformity of tube diameters in the laser oven. The question will be discussed in detail in the chapter "Growth mechanism of SWNTs".

**Catalyst metal**

Never were in the TEM catalytic particles observed directly attached to the ends of SWNTs. More general, no correlation between the location of catalytic particles and tubes was found at all. Most of the metal particles are enclosed in an amorphous carbon overcoating. The diameters of MWNTs grown from catalytic metal particles are clearly correlated with the size of the attached metal particle\cite{62, 63, 64} whereas no correlation between the size of catalytic particles and the diameter of SWNTs is found. In addition, the diameter of SWNTs produced using different metals seems to be independent of the kind of catalyst used. It thus appears that the tube diameter reflects an intrinsic property of the condensing carbon rather than a property of a particular carbon/metal cluster.
Growth mechanism of SWNTs

Based on the results so far described, an attempt will now be made to explain the formation of SWNTs in more detail. The central questions any growth mechanism will have to address is the nucleation of tubes and their uniformity of diameter. Other questions are the formation of ropes, the close termination of all tubes within a rope, and the lack of correlation between metal particles and tubes.

The metal scooter

Single-wall fullerene nanotubes are produced under conditions known to produce fullerenes in high yield in the absence of the transition metal catalyst. Thus, it is inevitable that fullerene-precursors are abundant in the early stages of SWNT growth. Accordingly, as has been argued before, SWNTs are likely an off-shoot of the road leading to C_{60}, nucleated from fullerene-precursors interacting with a metal vapor. Because of the high ratio of carbon to metal, and since carbon starts to condense at temperatures above 3000ºC, many of the carbon clusters initially formed will not include any metal at all. However, as condensation proceeds, there will be a small concentration of fullerene-precursors that one or several metal atoms have condensed on, interacting with the dangling bonds at the open edges of clusters. If the barrier between different sites on the edge is sufficiently small, the metal atoms will diffuse, or scoot, around the edge of the carbon cluster.

To introduce the pentagons necessary to grow into a fullerene, a carbon cluster always pays an energy cost due to the added strain of curvature compared with the alternative hexagons that would begin to form a straight tube 65. In addition, the introduction of pentagons often increases the number of truly dangling bonds at the edge (the chapter "The Bowl Road" will answer why this is so). Due to the requirement for such locally non
optimum structures, there is always a barrier to closure of a hemi-fullerene cap or a tubelet. Why do fullerenes grow at all? In the absence of a metal catalyst locally non optimum structures are frozen in at the edge until enough carbon has come in, and enough pentagons are included, to seal off the cluster.

Scooters effective at catalyzing the rearrangement of carbon rings will help to anneal away any carbon structures that are not the most energetically favored. That is, scooters will reanneal the edge to convert any locally non optimum structures into hexagons, lengthening the straight tube section and keeping the end of the just born tubelet completely open. Since the barrier to closure is never overcome, scooters redirect growth from fullerenes to tubes.

The residence time of a single metal atom will be limited at the elevated temperatures in the plume. At some point a single metal atom will desorb, allowing closure, unless its place is taken by another metal atom soon. However, once a couple of metal atoms are interacting with the dangling bonds, it is unlikely that the fullerene-precursor will ever find itself bare of metal again, and it can no longer close. This predicts that the tube yield will be a nonlinear function of the metal concentration, in agreement with the experimental observation that the tube yield rises dramatically over a very small concentration range and then levels off. Most likely then there are several metal atoms scooting around the open edge of the cluster.

**The diameter distribution**

The tubes forming as an off-shoot of the road leading to $C_{60}$ will initially grow with the same diameter as $C_{60}$, roughly 0.7 nm. For tubelets with such a small diameter, the strain energy in the cylinder will be high and accumulate very fast as tubelets grow longer. The strain energy would favor tubelets of larger diameter. However, the energy penalty for
dangling bonds located at the open edges of clusters will favor tubes of small diameter with a reduced number of dangling bonds. Thus, the optimum diameter is determined by competition between strain energy and dangling bond energy. Since the temperature is high enough to anneal and growing tubes are still small enough to rearrange to their most favored form, they will readjust as they add more carbon to form tubes of larger diameters, tolerating a slightly higher open edge energy. Beyond a certain size $N_{\text{crit}}$ however, clusters will finally have too many atoms to rearrange on the relevant time scale. At this time, their diameters get kinetically frozen due to shear size, even though they may continue to grow thousands of times as long. It is due to this ongoing competition that the diameter distribution ends up being so narrow.

The strain energy of a cylinder of diameter $D$ and length $L$ is $E_s = \varepsilon_c L/D$, where $\varepsilon_c = 15.1$ eV \(^{66}\). The strain energy $E_h$ of a hemi-fullerene is quite sensitive to the relative positioning of its six pentagons. For a hemi-fullerene with isolated pentagons and smooth curvature approximating a hemisphere though, $E_h = 10.3$ eV is to a very good approximation independent of diameter \(^{66}\). Finally, the energy stored in the dangling bonds at the growing edge is $E_e = \varepsilon_e \pi D$, where $\varepsilon_e = 21$ eV/nm has been estimated based on ab initio density functional calculations of a graphene sheet edge \(^{67}\). The total strain and edge energy $\Delta E$ of a tubule thus is

$$\Delta E = \frac{\varepsilon_c L}{D} + E_h + \varepsilon_e \pi D$$

Unfortunately, this expression is not easily interpreted, since a tubelet containing $N$ atoms will change its length as it adjusts its diameter. Let's thus replace $L$ with $N$, which is independent of $D$ for a given tubelet. The surface area $S$ of a tubelet is given by the surface area of the hemi-fullerene plus the surface area of the cylinder:
\[ S = \frac{\pi D^2}{2} + \pi DL \]

Multiplying \( S \) by the number of atoms per square area \( K = 0.38/\text{Å}^2 \) gives the number of atoms \( N \) contained in a tube of length \( L \) and diameter \( D \):

\[ N = SK = \frac{\pi D^2 K}{2} + \pi D L K \]

which is equivalent to

\[ \frac{L}{D} = \frac{N}{\pi D^2 K} - \frac{1}{2} \]

Substituting \( L/D \) gives the following expression for the strain/edge energy as a function of diameter \( D \) for a tube containing \( N \) atoms:

\[ \Delta E = \varepsilon_c \left( \frac{N}{\pi D^2 K} - \frac{1}{2} \right) + E_h + \varepsilon_e \pi D \]

Before considering this relation in detail however, it will be helpful to establish roughly at what size tubelets get kinetically locked. Using the fact that the strain/edge energy is minimized at the equilibrium diameter, we obtain a relation between the equilibrium tube diameter \( D_{eq} \) and the number of atoms \( N \). Using the experimentally determined diameter of 1.36 nm, we can then estimate \( N_{crit} \), the size of a cluster that finally can no longer rearrange.
\[
\left( \frac{\partial \Delta E}{\partial D} \right)_{eq} = -\frac{2 \epsilon_c N_{crit}}{\pi D_{eq}^3 K} + \epsilon_c \pi = 0
\]

or

\[
N_{crit} = \frac{\epsilon_c \pi^2 D_{eq}^3 K}{2 \epsilon_c}
\]

For the experimentally observed \( D_{eq} = 1.36 \text{ nm} \), \( N_{crit} = 680 \). Considering the fact that the energy of the open edge will be lowered by interaction with the metal catalyst, \( N_{crit} \) will actually be somewhat smaller. Clusters continue to adjust their diameter as they grow bigger until they are no longer able to do so by the time they contain several hundred atoms. We can now go back and plot the strain/edge energy for tubelets of various sizes as a function of diameter (see Figure 14).
Figure 14: Strain/edge energy of tubelets as function of diameter

Strain/edge energy of tubelets per atom ($\Delta E/N$) as function of diameter $D$ for tubelets containing 300, 500, and 700 atoms.
The armchair edge

In the previous section it has been shown how due to competition between strain energy and dangling bond energy tubes with a diameter close to 1.36 nm are favored. Still, this would predict that a vast variety of different kinds of tubes are present in the felt, since many tubes with different helicities can be found to closely match any given tube diameter. It will now be shown via a more detailed consideration of the edge geometry how a selected class of tubes is favored: zero helicity tubes with an armchair edge.

Figure 15 demonstrates how the different arrangement of dangling bonds on a zigzag edge and an armchair edge affects their relative stability. Figure 15a shows that a zigzag edge is the least favorable possible geometry for an open edge of a graphene sheet: The dangling bonds on a zigzag edge are separated by an intermediate atom. This intermediate atom prevents any favorable interaction between dangling bonds. In this sense, a zigzag edge has true dangling bonds. Figure 15b shows the opposite extreme: On an armchair edge, dangling bonds always come in pairs on adjacent atoms. These neighboring dangling bonds on the armchair edge can interact to form triple bonds, thereby significantly reducing the penalty due to unsatisfied bonds.

Figure 15: Zigzag edge (left) and armchair edge (right)
At this point it is useful to remark that any nanotube can be denoted by a pair of indices \( (n,m) \) \(^{68}\). These indices contain all the information necessary to deduce the diameter as well as the helicity of the nanotube. Nanotubes can be constructed by rolling a planar graphene sheet into a cylinder. In this process, hexagons located at the endpoint of vector \( \mathbf{R} = nx + my \) are superimposed onto hexagons located at the origin of vector \( \mathbf{R} \). The tube defined in this manner is named \( (n,m) \) tube. Here \( \mathbf{x} \) and \( \mathbf{y} \) are the primitive vectors of the graphene sheet oriented at an angle of 60 degree to each other with length \( \sqrt{3} d_{cc} \) and \( (n,m) \) is the integral set satisfying the conditions \( n > m, n \geq 1, m \geq 0 \). \( d_{cc} \) is the carbon-carbon bond length. Zero helicity armchair tubes are those for which \( n = m \).

**The buckyball of tubes**

Combining the notion that armchair tubes are most favored with the experimentally observed mean tube diameter of 1.36 nm, one has to conclude that the \( (10,10) \) tube is the single most prominent tube in the felt under annealing conditions: The \( (10,10) \) tube is of armchair geometry and matches the observed diameter perfectly! Because of its dominance in SWNT samples prepared by laser vaporization, the \( (10,10) \) tube can be referred to as the “buckyball of nanotubes”. Just as \( C_{60} \) is the favored form of carbon under conditions constraining carbon clusters to remain nanoscopic, the \( (10,10) \) tube is the best solution if the carbon cluster is constrained to remain open beyond the point when it would have normally closed into a fullerene. The \( (10,10) \) tube is for tubes what \( C_{60} \) is for balls.

Figure 16 shows a young \( (10,10) \) tubelet. Note the open armchair edge with a scooter attached to it, while the other end of the tubelet is sealed off by a hemi-fullerene cap. At this point it should be noted how the high symmetry of the \( (10,10) \) tube and its cap renders the \( (10,10) \) tube unique among nanotubes. Since tubelets start out with a cap where radial pentagons are separated from the central pentagon by only one 6-6 bond.
half of a C$_{60}$ fullerene, the 5 radial pentagons must move outward while the tube widens its diameter to form the cap seen in the image, half of a C$_{240}$ fullerene. Nickel and cobalt atoms or small carbon radicals$^{69}$ diffusing over the surface of the growing tubelet will likely help such rearrangements throughout the initial growth period until the final diameter of the tube is established. Due to its high symmetry resulting from the even spacing of all six pentagons, the C$_{240}$ cap can be expected to have a lower strain energy than any alternative geometry to seal off a (10,10) tube. Since accordingly the majority of (10,10) tubes should possess identical caps, the (10,10) tube provides a nanoscale tip exactly defined at an atomic scale. The center of the hemi-fullerene dome is formed by a corannulene like C$_{20}$ structure. Later it will turn out that this is more than just cute.
Figure 16: (10,10) tubelet with a scooter
The notion that armchair tubes are favored can be put on more quantitative grounds by comparing the relative edge energies of a (10,10) tubelet with other tubelets of similar diameter, but different edge geometry. The (11,9) and (12,8) tubelets can be expected to be close competitors, having only up to 2 and up to 4 dangling bonds, respectively (the exact number of dangling bonds depends on the particular arrangement of the section in the edge that is not armchair). For comparison, the edge energy of a (17,0) tubelet, the zigzag tubelet closest in diameter to the (10,10) tube, is also calculated. Since these tubelets have nearly identical diameter, only the difference in edge energy will affect their relative abundance. The edge energy of a carbon nanotube of helicity indices \((n,m)\) and diameter \(D = 0.78\sqrt{n^2 + nm + m^2}\) is roughly

\[
E_e = (\varepsilon_{db} N_{db} + \varepsilon_{tb} N_{tb})
\]

where \(N_{db} = n - m\) is the number of two-coordinated edge atoms that have a dangling bond, and \(N_{tb} = 2m\) is the number of two-coordinated edge atoms that are involved in triple bonds. Rough estimates for the dangling bond \((db)\) and triple bond \((tb)\) energies per atom are \(\varepsilon_{db} = 2.9\) eV and \(\varepsilon_{tb} = 2.1\) eV from tight binding calculations\(^{70}\), and \(\varepsilon_{db} = 2.8\) eV and \(\varepsilon_{tb} = 2.0\) eV from local density functional calculations\(^{71}\). In the following comparison (see Table 6), the lower density functional values are used.

<table>
<thead>
<tr>
<th>Tube</th>
<th>diameter / nm</th>
<th>(E_e) / eV</th>
<th>(\Delta E) / eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>(10,10)</td>
<td>1.351</td>
<td>40</td>
<td>0</td>
</tr>
<tr>
<td>(11,9 )</td>
<td>1.353</td>
<td>41.6</td>
<td>1.6</td>
</tr>
<tr>
<td>(12,8 )</td>
<td>1.360</td>
<td>43.2</td>
<td>3.2</td>
</tr>
<tr>
<td>(17,0 )</td>
<td>1.326</td>
<td>47.6</td>
<td>7.6</td>
</tr>
</tbody>
</table>

Table 6: Relative energies for various SWNTs
The closest competitor of the (10,10) tube pays an energy penalty of 1.6 eV due to the less favorable geometry of its edge. At an annealing temperature of 1200°C the Boltzmann factor for a 1.6 eV excitation is about $3 \times 10^{-6}$. Thus it seems reasonable that under annealing conditions most of the clusters could find to the (10,10) geometry. A final concern might be that only a (10,10) tube with a complete rank of hexagons around the tube will have no dangling bonds, while a partly finished rank will have at least one true dangling bond that cannot participate in triple bonding. Still, the (10,10) tube will even be favored when growing a new rank thanks to the low strain energy in its cap.

The realization that most tubes can be expected to be of the armchair geometry also means that most tubes will have a lower edge energy than the previously used average edge energy of $\varepsilon_e = 21$ eV/nm. Accordingly, $N_{crit}$, the cluster size at which tubes can no longer readjust their diameter, has to be reevaluated, since it is a function of the edge energy. The edge energy of a (10,10) tube, just calculated to be $E_e = 40$ eV, corresponds to $\varepsilon_e = E_e / \pi D = 10$ eV/nm. This means that a (10,10) tubelet should have reached its final diameter at a cluster size of $N_{crit} = 326$.

The ability to produce samples with a narrow diameter distribution centered around the (10,10) tube, dominated by armchair geometry tubes, is significant progress if nanotubes are to gain importance as practical materials: After presenting the synthesis of SWNTs in the laser-oven-setup, it was pointed out that fixing the number of walls to one was an important step towards the production of well defined nanotube materials. After gaining control over the number of concentric shells, now it is clear that to a large degree both tube diameter and tube helicity can be controlled.
Growth of ropes

The short tubelets formed during the initial phase of the clustering process inevitably collide in the gas phase and start to align with each other due to van der Waals interaction. Soon every tube is part of a rope, and much of tube growth occurs subsequently. That formation of ropes takes place very early in the growth process becomes strikingly clear when considering the alternative: Ropes couldn't possibly grow to their full length first and then align, since tubes thousands of times longer than their diameter would surely get caught in a tangled mess.

Feedstock for the SWNTs arrives at the "live" ends mostly by diffusion of carbon clusters along the sides of the tubes. When a SWNT is in contact along the side of a longer rope, it receives additional feedstock diffusing down the rope from the front, and its growth accelerates until it catches up with the longest SWNT in this direction of the rope (which is growing more slowly because it can only receive feedstock from the rear). This way, all tube-ends remain close during growth.

The catalytic particle

It has been argued before that the presence of catalytic metal particles rather than individual atoms is required at later stages of growth to explain the positive effect of bimetallic catalyst mixtures on the nanotube yield. Because the binding energy per atom for a small cluster containing a few metal atoms is substantially lower than that for the bulk metal, initially metal atoms are most likely to interact individually with the carbon edge rather than to form a metal cluster. However, as the number of metal atoms increases, they will coalesce into a catalytic particle. The role of such a catalytic particle is to digest incoming large carbon structures, for example fullerenes, and include additional carbon between itself and the nanotube attached to it. Considering that tubes
grow to lengths $10^5$ times their diameter, one might even say that the little metal particles feed their nanotubes at a frenzied speed. Even if such metal particles grew at some point during condensation beyond the diameter of the SWNTs attached to them, continued growth of a single layer of carbon hexagons will still be favored: While the lower strain energy of a second layer precipitated from a larger metal particle would be energetically favored compared with adding to the inner layer, the unavoidable open edges introduced as this second layer nucleates would present a high energetic barrier.  

The postulation of such catalytic particles however gives rise to another question: Why has no metal particle ever been observed attached to the end of a SWNT grown in the laser oven? Apparently, the catalytic particle is lost at some stage. Any attempt to explain this observation also needs to account for the fact that all tubes in one rope terminate close to each other. Either one of the following two mechanisms seem to offer a plausible explanation:

The first model goes by the name "fatness": While tubes grow by including carbon at their live ends, metal will also deposit onto the tubes. At least part of this metal will diffuse to the growing ends of tubes. Here it will become part of a growing catalytic particle. Initially, such a particle suffers a huge penalty due to its large fraction of surface atoms and will profit substantially from interaction with the carbon dangling bonds. As the cluster grows however, the number of surface atoms able to lower their energy via interaction with the carbon cluster remains constant, while the total number of surface atoms increases. Accordingly, the importance of the metal carbon interaction in the energy balance of the metal particle decreases. More importantly, the binding energy per metal atom approaches that of the bulk, as the fraction of surface atoms in the metal cluster decreases. At some point, it will no longer be energetically advantageous for the metal cluster to remain attached to the end of the tube. Metal cluster and tube separate, sealing off the end of the tube with a hemi-fullerene cap in the process. This suggested separation of a catalytic particle from its tube due to fatness is analogous to the observed
closure of MWNTs by small metal particles. Once the first metal particle has come off the end of its tube, it will sample around and most likely find other catalytic particles still attached to their tubes, since all tube-ends within a rope are close to each other. The encounter of metal particles should then result in their coalescence to form a bigger metal particle, sealing off another tube. This coalescence of individual catalytic particles causes the almost simultaneous termination of growth for all tubes at the end of a rope. This separation of metal particles and tubes would also offer a straightforward explanation for the drop in tube yield as the metal concentration is increased beyond roughly 2 or 3% by mole: Since metal particles grow even faster, tube growth will terminate earlier at higher metal concentrations. There is one serious drawback to this model, however: An upper limit for the size of catalytic particles during growth can be obtained by assuming that the ratio of metal to carbon in the feedstock is the same as in the starting material, roughly 1 to 100, and that one metal atom is added to the catalytic metal particle for every 100 carbon atoms included into a nanotube. The catalytic particle has grown to about the same diameter as the nanotube by the time the nanotube is about 100 nm long. In the highest yield samples, tubes might well be 100 μm long. By this time, the catalytic particle should be about 10 nm in diameter. However, it is very unlikely that particles of this size would stay attached to tubes, they would likely have fallen off much earlier, terminating growth at a stage when tubes are much shorter than what is actually observed. Apparently, "fatness" is not the whole truth.

Alternatively, the lack of any spatial correlation between tube-ends and metal particles can be explained by the evaporation of metal particles off tube-ends after condensation comes to a halt: It appears that some effect causes the catalytic metal particles to stay small during growth, allowing tubes to grow to the observed length. Three effects are likely to contribute: (1) Not all the feedstock coming to the catalytic particle carries its share of metal. Fullerenes, certainly abundant in the gas phase, may not bring any metal at all. (2) Most carbon as well as metal will first deposit on the sides of ropes. While carbon is mobile enough to eventually find the growing ends of ropes, much of the metal may
accumulate in the crevices formed between tubes or at intersections of ropes and never make it to the growing ends. (3) Finally, and possibly most importantly, metal constantly evaporates from catalytic particles due to the enhanced vapor pressure of small particles and accumulates in bigger particles, which get enclosed by carbon. Consequently, catalytic particles attached to the ends of tubes remain relatively small during growth due to a balance between metal carried to the catalytic particle by feedstock and metal lost due to evaporation. The tubes in a rope then all run out of feedstock at the same time and terminate close to each other because throughout growth shorter tubes always catch up with longer tubes. After all feedstock is consumed, the metal present in catalytic particles eventually evaporates completely and the ends of tubes anneal into a dome.

Both scenarios also explain why there has been no observed correlation between nanotube diameter and size of the metal particles in the final felt. The metal particles observed in the TEM are simply not the catalytic particles that were once attached to nanotubes.
Characterization

Helicity

First evidence that the armchair geometry is indeed favored came from electron diffraction. The absence of any strongly preferred alignment of ropes makes it difficult to derive the helicity of tubes by conventional electron microscopy. This problem was circumvented by taking advantage of the nanodiffraction capabilities of a scanning transmission electron microscopy (STEM) instrument \(^{74}\), which allowed diffraction patterns to be obtained from any region, 1 nm or less in diameter, selected from either a bright-field or dark-field image. The STEM instrument used was an HB-5 from VG Microscopes Ltd. modified by addition of a high-resolution objective lens pole-piece and a special detector system for recording diffraction patterns by use of a low-light-level TV camera and VCR system or a CCD camera with digital data-handling system \(^{75}\). To study the nanotubes, an electron beam of diameter 0.7 nm was either held stationary at a chosen spot within the dark-field image of a rope or else was scanned rapidly over an area of the rope, 10-20 nm in diameter, during the recording time, in order to give an indication of the average structure of the nanotubes within the rope.

Some simple considerations allow to construct the diffraction pattern to be expected for a rope containing exclusively armchair tubes, assuming 0° tilt of the rope with respect to the incident beam. Diffraction from a three-dimensional crystal can be rationalized as originating from a set of planes of atoms. In the case of a two-dimensional object like a graphite sheet, it is easiest to think of diffraction as originating from a set of lines of atoms. The graphene walls of a SWNT can be treated as such a two-dimensional object. Lines of carbon atoms within the walls of a tube giving rise to diffraction spots along or at an angle to the tube axis. The following discussion refers to Figure 17. A graphene sheet is defined by two equal axes \(a\) and \(b\) at an angle of 120°. Interference from lines of atoms
parallel to these axes gives rise to the 1,0 and 0,1 reflections. The diffraction spots are in
directions perpendicular to these lines and so are at 60° to each other. The 1,1 reflection
stems from the parallel set of lines of atoms at 30° to the axes (parallel to the line through
the end points of the axes). Again the diffraction spot is indirection perpendicular to these
lines, thus it is in direction of the tube axis. Due to the nature of interference, the spacing
of a particular diffraction spot from the origin is inversely related to the separation
between the set of parallel lines giving rise to this spot. Thus, the 1,1 spot is spaced
further out from the origin than the 1,0 and 0,1 spots. To produce spots of observable
intensity, interference of a large number of lines of atoms is necessary. This requirement
is only met for lines of atoms perpendicular or almost perpendicular to the tube axis, as is
ture for the 1,1 spot or the 1,0 and 0,1 spots. Since armchair tubes are zero helicity,
diffraction spots for the top and bottom sheets of any armchair tube coincide.

Figure 17: Expected diffraction pattern for armchair tubes
Diffraction patterns and corresponding images were recorded for a total of 35 ropes. Regions of the ropes were selected to exclude those too obviously bent, twisted, tilted with respect to the beam, or contaminated with amorphous or other extraneous material. The rope diameters varied from 3 to 30 nm. 9 of these ropes showed an exact 0° helix angle with no appreciable spread of helicities. (For convenience, the following discussion will refer to armchair tubes as having 0° helicity.) Figure 18 shows a diffraction pattern from one such rope apparently made up completely from armchair tubes: The bright line results from the lateral stacking of tubes within the rope. The tube axis is oriented perpendicularly to this line. Clearly visible are the 1,0 and 0,1 diffraction spots at a 30° angle from the tube axis, which are characteristic for armchair tubes, as well as the 1,1 diffraction spots coinciding with the tube axis.

Figure 18: Electron diffraction pattern from a pure armchair rope

For all ropes except 2, the predominant helicity, shown by the averaged diffraction patterns obtained with the beam scanned over the rope, was around 0°. For one narrow
rope the helicity was 30° away from this, and for one rope there was a mixture of 30° and 0° helicities. 4 ropes showed a strong preference for a helicity of 5° away from 0°; 5 ropes showed a spread of helix angles from 0° to about 5° (as indicated by the continuous arcing of the diffraction spots); 12 ropes showed a spread of helix angles of up to about 10°. There was no obvious correlation between the values or spreads of helix angles and the rope diameter.

The nanodiffraction patterns confirm that armchair tubes are energetically favored and occur most frequently. The helix angles of about 5° and 10°, which are also found with relatively high probability might correspond to the (11,9) and (12,8) configurations, for which the helix angles differ from the (10,10) tube by 5° and 9.5°, respectively. Both these tubes come very close to ideal armchair tubes in the sense that the edge of an (11,9) tubelet contains only up to 2 dangling bonds, while the edge of a (12,8) tubelet contains only up to 4 dangling bonds, all remaining 2-coordinated atoms on the open edge participating in triple bonds. If it is assumed that the ropes showing an average pattern with a spread of up to 5° consist of an equal mixture of (10,10) and (11,9) tubes, and those ropes showing an average pattern with a spread of up to 10° consist of equal parts (10,10), (11,9), and (12,8) structures, then the particular sample under study contained a mixture of 44% (10,10) tubes, 30% (11,9) tubes, and 20% (12,8) tubes.

At this point, a note of caution is in place. The experimental confirmation that armchair tubes are dominant in laser generated samples puts the scooter mechanism on even more solid ground. It does not mean though that the scooter mechanism is the only possible way to nucleate SWNTs. It has been found that SWNTs can also be synthesized from preformed metal particles, as described in Appendix "SWNTs from preformed catalytic particles". In this process, most likely zigzag tubes are favored.
**Tube-tube fusion**

The just presented electron diffraction results could be obtained for as grown felt material, since none of the contaminants present in the felt like amorphous carbon or nanometer sized metal particles interfered with these experiments. Eventually though, the presence of contaminants has to pose a serious problem for further characterization of the ropes. To prepare a sound basis for future investigations, an effort was undertaken to remove the various contaminants present in the felt. The first step was actually taken when fullerenes were sublimed out of the felt at 1000°C in preparation for XRD. Considering that Co and Ni have melting points of 1495°C and 1453°C, respectively, heat treatment at an appropriate higher temperature should remove the metal present in the felt in addition to fullerenes. Indeed, material baked under vacuum at 1500°C for 30 minutes was found to be almost completely deprived of its original metal content. However, a problem stems from the catalytic activity of the metals to be removed: Figure 19 suggests that metal enclosed in graphitic layers of an imperfect onion at the outset of the heat treatment actually catalyzes the onion to perfection during the heat treatment, which leaves some fraction of the metal entrapped in a now perfect onion.
Figure 19: Metal left behind in a perfected onion
A more careful inspection of the material after heat treatment at 1500°C gave rise to another concern. It was observed that some tubes appeared to have a much larger diameter, often along their whole length, than typical for the samples. Could it be that tubes, only metastable against structures with lower curvature, coalesced to form tubes of larger diameter in order to relieve some of their strain energy?

The possibility that fullerenes coalesce was first suggested 37 in 1991 to explain the appearance of increasing amounts of $M_x@C_n$, with 2-4 metal atoms and $n > 100$, as nascent metallofullerenes react with one another between successive laser vaporization shots of a composite graphite/metal target. Subsequently, coalescence of empty fullerenes was also reported 77. Coalescence of tubes over long stretches would be inconceivable from the outset were it not for the remarkable tendency for individual nanotubes to align over their entire lengths. However, in order for tubes to coalesce seamlessly over great lengths, they must also have the same chirality and helical pitch angle. Thus, coalescence on a large scale would be out of question for samples containing SWNTs with random helicities. For samples with a significant fraction of armchair tubes however, a large number of neighboring tubes would possess the same helicity (and the same chirality since armchair tubes are achiral), and many if not most of the tubes in a sample could potentially coalesce.

In order to clarify the origin of the observed tubes with extraordinary large diameter, samples of SWNT material were placed in a ceramic boat in a 2" alumina flow tube and treated at either 1400°C or 1500°C within a tube furnace (Lindberg) under various atmospheres 78. The level of potentially chemically active gases like hydrogen, water, and their equilibrium products at the relevant temperatures ranged from medium high vacuum to 8 mtorr. In addition to 1.36 nm diameter tubes, TEM micrographs of SWNTs so annealed always showed tubes 2.7 nm in diameter, twice the (10,10) tube diameter. A few tubes with three times the diameter of the (10,10) tube were also observed, but they are relatively rare. The amount of doubled tubes correlated with the level of
background gases, and ranged from 5% to 60%. In general, annealing always results in a bimodal distribution, with one peak centered on the (10,10) tube diameter of 1.36 nm, and the other centered at about twice this diameter.

These results suggest that SWNT coalescence is initiated by a gas phase species attacking the side of a nanotube to break a C-C bond, producing a defect in an otherwise perfect graphene network. Either the original attacking species or the newly formed reactive carbon edge atoms can subsequently attack a neighboring tube, producing a defect in the second tube. Once these adjacent defects have formed, there is no energetically advantageous way for 2 tubes to connect locally (e.g., by forming a seamless bridge between them). There will be a strong thermodynamic driving force however, resulting from the reduced strain energy of larger diameter tubes, for the two neighboring tubes to join together. After zipping begins, this driving force will impel the 2 tubes to knit together for as long as they run together. In this process of joining two tubes together, the 2 opposing defects propagate along their mutual lengths while zipping closed the graphene sheets into one large tube in their wake.

Recalling that the strain energy within the cylinder of a nanotube is $E_c = \varepsilon_c L/D$, where $L$ is the length of a tube of diameter $D$ and $\varepsilon_c = 15.1$ eV, the enthalpy change for coalescence of two (10,10) tubes into one (20,20) tube is huge, approximately 16.6 eV/nm. Larger diameter tubes should be less susceptible to coalescence for 2 reasons: (1) Even though it is energetically favorable for tubes to relieve strain at any diameter, the coalescence exothermicity of smaller diameter tubes is greater than for larger diameters. The enthalpy change is 20% smaller for coalescence of a (20,20) tube and another (10,10) tube to yield a diameter-tripled tube. This trend towards smaller exothermicities continues for higher-order coalescence. (2) Probably more importantly, coalescence of tightly wound tubes is kinetically favored: Since curvature introduces more s-character into the $\pi$-orbitals, the reactivity of a curved graphene sheet increases as the tube diameter becomes smaller. In
accordance with these considerations, very little coalescence of larger-diameter tubes was observed.

For two tubes to knit together seamlessly, they must have the same helical pitch angle and chirality, otherwise they immediately lose their registry, making the distance between open edges too great to bridge. For a sample of nanotubes with random helicities it is very unlikely that these conditions will be fulfilled for many pairs of neighboring tubes. This does not preclude other types of chemistry between unmatched carbon networks, like formation of bridges between tubes, but significant numbers of coalesced tubes cannot be obtained in such samples.

The observed high percentage of coalescing SWNTs therefore argues strongly for the converse: that the starting material is dominated by nanotubes of a single helicity. The observed ~60% maximum conversion provides rather dramatic additional evidence that a large fraction of nanotubes have the same pitch angle and chirality. The simplest way to have both properties be the same is to be achiral, i.e., zero-helicity. This of course would be true for samples dominated by armchair tubes.

**Metallic resistivity of ropes**

The point that the armchair geometry is most favored has been made by now. Why is this important? The answer is as simple as it is dramatic: Most tubes are either moderate gap or small gap semiconductors at best. Armchair tubes are the only class of tubes that are truly metallic!

Evidence for metallic behavior of the tubes generated in the laser-oven-setup was first obtained by means of electron spin resonance experiments. A first attempt showed an intense line with a linewidth $\Delta H \sim 400$G at 300K due to the presence of the ferromagnetic
catalyst residues. Vacuum annealing at 1500°C for 30 minutes at 10^{-6} torr eliminated this line as well as the XRD peaks characteristic of Co-Ni, and the sample was no longer attracted to a permanent magnet. After this heat treatment, only a narrow Dysonian line with a Landé factor \( g = 2.001 \pm 0.001 \) was observed; this value is characteristic of a metal for which the skin depth (at 10 GHz) is less than the sample dimensions (see Figure 20). For comparison, polycrystalline graphite exhibits a line that is typical of a powder spectrum with an anisotropic \( g \) factor \((g_\parallel = 2.035 \text{ and } g_\perp = 2.009)\), whereas a sample of amorphous carbon derived from coal pitch gives a symmetric (non-Dysonian) line near \( g = 2 \) with a peak to peak line width \( \Delta H_{pp} = 40 \text{ G} \). The only previous ESR measurement on oriented MWNTs \(^7\) yielded a symmetric line whose temperature dependence and magnitude and anisotropy of \( g \) were consistent with those of small, graphite-like semimetallic particles.
Figure 20: ESR of SWNT material
Dresselhaus et al. \textsuperscript{80} obtained a general expression for the bandstructure of armchair tubes from the dispersion relation for a single graphene sheet. Their approach combines a tight binding level description of the $\pi$-band, considering contributions only of p-orbitals, with the periodic boundary condition imposed by the finite dimension of tubes along their circumference. It is predicted that all armchair tubes are metallic, since for any armchair tube two bands cross the Fermi level.

It is instructive to consider how the properties of extended tubes arise from their molecular building block, the unit cell. The following discussion will show how symmetry underlies the metallic character of armchair tubes. It is also a beautiful example for the intimate relation of concepts typically used in connection with quite distinct systems, namely, the description of the electronic properties of individual molecules in terms of molecular orbitals, and the description of the electronic properties of extended solids in terms of crystal momentum. The following discussion is based on the (5,5) tube as an example of tractable size, but the results apply to armchair tubes in general. The unit cell of any armchair tube consists of a belt containing pairs of carbon atoms alternately below and above a plane oriented perpendicularly with respect to the tube axis (the z-direction) (see Figure 21). The radially extending p-orbitals, one on each carbon atom, can be combined into molecular wavefunctions, the symmetry adapted linear combinations of atomic orbitals (SALCs). A tube can be built by repeated translation of the unit cell along the tube axis. Similarly leads the repeated translation of SALCs to wavefunctions extending along the entire tube. Modulation of SALC-based wavefunctions in the z-direction, giving rise to longitudinal crystal momentum, then leads to a set of Bloch wavefunctions extending over the entire tube, in which the angular nodal pattern of the underlying SALCs is retained. The amplitude oscillation of the Bloch wavefunctions is described by the crystal momentum quantum number $k$, which can range from $-\pi/a$ to $+\pi/a$. 
Figure 21: Unit cell of the (5,5) tube

The unit cell of the (5,5) tube is obtained by closing the chain of 20 carbon atoms into a belt.

The unit cell of the (5,5) tube has $D_{5d}$ symmetry. The reducible representation based on one radially directed p-orbital per carbon atom in the unit cell, $\Pi$, is particularly simple, since the identity is the only symmetry operation that takes a particular p-orbital into itself:

<table>
<thead>
<tr>
<th>$D_{5d}$</th>
<th>E</th>
<th>$2C_5$</th>
<th>$2C_5^2$</th>
<th>$5C_2$</th>
<th>$i$</th>
<th>$2S_{10}$</th>
<th>$2S_{10}^3$</th>
<th>$5\sigma_d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_{1g}$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$A_{2g}$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>$E_{1g}$</td>
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<td>-b</td>
<td>0</td>
<td>2</td>
<td>a</td>
<td>-b</td>
<td>0</td>
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<tr>
<td>$E_{2g}$</td>
<td>2</td>
<td>-b</td>
<td>a</td>
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<td>1</td>
<td>1</td>
<td>1</td>
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<td>-1</td>
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<tr>
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<td>a</td>
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<td>-a</td>
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</tr>
<tr>
<td>$\Pi$</td>
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<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 7: $D_{5d}$ character table (a = 0.618034, b = 1.618034)

$\Pi$ decomposes into the following irreducible representations (irreps), corresponding to 20 states, as required for a basis consisting of 20 p-orbitals:
\[ \Pi = A_{1g} + A_{2g} + A_{1u} + A_{2u} + 2E_{1g} + 2E_{2g} + 2E_{1u} + 2E_{1u} \]

It is now necessary to find the appropriate linear combinations of p-orbitals that transform as irreps of the point group (for the unit cell) and of the space group (for the infinite tube). These combinations are the symmetry adapted linear combinations of atomic orbitals (SALCs). In order to find SALCs, the effect of the symmetry operators \( \hat{R} \) on selected p-orbitals must be established. In the following, p-orbitals are denoted by bold figures 1 through 20.

| \( \hat{R} \) | E | C_5 | C_5^2 | C_5^3 | C_5^4 | C_2 | C_2^* | C_5^r | C_5^l | i | S_{21} | S_{21}^{-1} | S_{31} | \sigma_d | \sigma_d | \sigma_d | \sigma_d |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| \( \hat{R} \) (1) | 1 | 5 | 17 | 9 | 13 | 2 | 6 | 10 | 14 | 18 | 11 | 3 | 19 | 7 | 15 | 4 | 8 | 12 | 16 | 20 |
| \( \hat{R} \) (2) | 2 | 6 | 18 | 10 | 14 | 1 | 5 | 9 | 13 | 17 | 12 | 4 | 20 | 8 | 16 | 3 | 7 | 11 | 15 | 19 |
| \( \hat{R} \) (3) | 3 | 7 | 19 | 11 | 15 | 20 | 4 | 8 | 12 | 16 | 13 | 5 | 1 | 9 | 17 | 2 | 6 | 10 | 14 | 18 |
| \( \hat{R} \) (4) | 4 | 8 | 20 | 12 | 16 | 19 | 3 | 7 | 11 | 15 | 14 | 6 | 2 | 10 | 18 | 1 | 5 | 9 | 13 | 17 |

Table 8: Effect of symmetry operators on selected p-orbitals

SALCs for 1-D irreps can be found by applying the projection operator \( \hat{P}_{\text{irrep}} \) on a single p-orbital as generating vector (no normalization):

\[
\hat{P}_{A_{1g}}(1) = 1+2+3+4+5+6+7+8+9+10+11+12+13+14+15+16+17+18+19+20
\]
\[
\hat{P}_{A_{2g}}(1) = 1-2+3-4+5-6+7-8+9-10+11-12+13-14+15-16+17-18+19-20
\]
\[
\hat{P}_{A_{1u}}(1) = 1+2-3+4+5+6-7+8+9+10-11+12-13+14-15-16+17+18-19-20
\]
\[
\hat{P}_{A_{2u}}(1) = 1-2+3-4+5-6+7-8+9-10+11-12+13-14+15-16+17-18+19+20
\]

Since \( \Pi \) contains each 2-D irrep twice, two pairs of degenerate SALCs, or four SALCs, need to be obtained for each 2-D irrep. These all need to be mutually orthogonal, of course. For this it is necessary to apply the projection operator \( \hat{P}_{\text{imp}} \) to different
generating vectors. In this case, the generating vectors are easy enough to guess, for example 1 through 4. For the \( E_{1g} \) irrep, the SALCs are (no normalization):

\[
\hat{\rho}_{E_{1g}}(1) = 2\times 1 + a\times 3 + a\times 5 - b\times 7 - b\times 9 + 2\times 11 - b\times 13 - b\times 15 + a\times 17 + a\times 19 \\
\hat{\rho}_{E_{1g}}(2) = 2\times 2 + a\times 4 + a\times 6 - b\times 8 - b\times 10 + 2\times 12 - b\times 14 - b\times 16 + a\times 18 + a\times 20 \\
\hat{\rho}_{E_{1g}}(3) = a\times 1 + 2\times 3 + a\times 5 + a\times 7 - b\times 9 - b\times 11 + 2\times 13 - b\times 15 - b\times 17 + a\times 19 \\
\hat{\rho}_{E_{1g}}(4) = a\times 2 + 2\times 4 + a\times 6 + a\times 8 - b\times 10 - b\times 12 + 2\times 14 - b\times 16 - b\times 18 + a\times 20
\]

SALCs for the other 2-D irreps can be obtained in analogous fashion. The energetic order of the SALCs or Bloch wavefunctions at the zone center (k\( \times a = 0 \)) can then be deduced from their angular nodal pattern. Alternatively, the energetic order can be deduced from the bond order. The wavefunctions can schematically be represented in an amplitude diagram. Figure 22(top) shows the sign of the wavefunctions based on SALCs transforming as 1-D irreps for the first four atoms in two adjacent unit cells, respectively, at the zone center (k\( \times a = 0 \)). The pattern repeat over the remainder of the unit cells. Since the bond orders are 3 for \( A_{1g} \), 1 for \( A_{1u} \), -1 for \( A_{2u} \), and -3 for \( A_{2g} \), the energy increases in the order \( A_{1g} < A_{1u} < A_{2u} < A_{2g} \).

Figure 22(bottom) shows the sign of the wavefunction for the 1-D wavefunctions at the zone edge (k = \( \pm \pi/a \)). Now \( A_{1g} \) and \( A_{2u} \) have the same bond order, 1, and are degenerate, and \( A_{1u} \) and \( A_{2g} \) have the same bond order, -1, and are degenerate. The energetic order of the 1-D wavefunctions at the zone edge is thus \( A_{1g} = A_{2u} < A_{1u} = A_{2g} \). Note that \( A_{2u} \) and \( A_{1u} \) switched places compared to the zone center, meaning that the two bands based on SALCs labeled \( A_{2u} \) and \( A_{1u} \) have to cross at some point \( -\pi/a < k < 0 \).

Comparison with the complete bandstructure shows that the 2 bands generated from the \( A_{1u} \) and \( A_{2u} \) wavefunctions are partially filled and cross the Fermi level at k = \( 2\pi/3a \).
<table>
<thead>
<tr>
<th>zone center</th>
<th>bo = 3</th>
<th>bo = 1</th>
<th>bo = -1</th>
<th>bo = -3</th>
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<tbody>
<tr>
<td>unit cell 1</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>unit cell 2</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>zone edge</th>
<th>bo = 1</th>
<th>bo = 1</th>
<th>bo = -1</th>
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<tr>
<td>unit cell 1</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>unit cell 2</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
</tbody>
</table>

Figure 22: Amplitude diagram

Amplitude diagram for 1-D wavefunctions at the zone center (top), and the zone edge (bottom). Also indicated are the bond orders (bo). Energy of the wavefunctions increases with bond order from left to right. The arrows indicate the band crossing arising from the different energetic order of wavefunctions at the zone center and zone edge.

Consideration of the Brillouin zone (BZ) of a graphite sheet also allows to predict the metallic character of armchair tubes, as shown by Hamada et al. \(^81\). The bonding and antibonding \(\pi\)-bands are degenerate at the K-point in the BZ of a graphite sheet \(^82\), \(^83\). For a tubule, while the boundary condition along the tube axis is the same as for graphite, a periodic boundary condition is imposed for a finite period along the circumference. This results in sets of Bloch wave functions with discretely selected wave vectors. Each set of Bloch wave functions has fixed angular momentum within the surface of the tube, but varying longitudinal crystal momentum, and contains all Bloch wave functions that can be generated via modulation of one SALC by longitudinal crystal momentum ranging
from $-\pi/a$ to $+\pi/a$. The endpoints of wave vectors corresponding to wave functions with identical angular momentum lie on straight lines cutting through the BZ parallel to the tube axis. The relative orientation of the graphite sheet with respect to the tube axis determines whether or not there will be wave vectors whose endpoints coincide with the K-point. For any tube do 2 sets of wave vectors exist that end on a line through the center of the BZ. (For the (5,5) tube, wave vectors based on the SALCs transforming as $A_{1u}$ and $A_{2u}$, which were classified as crossing the Fermi energy, end on the line going through the center of the BZ.) For armchair tubes, this line always intersects the K-point, where bonding and antibonding $\pi$-bands are degenerate, since for armchair tubes the line connecting the center of the BZ with the K-point is also parallel to the tube axis. For any other tube geometry, the line through the center of the BZ does not intersect the K-point, the remaining lines representing endpoints of wave vectors, however, may intersect the K-point accidentally. This approach may be the easiest way to demonstrate the special position taken by armchair tubes purely from symmetry considerations. If the $\pi$-band is treated as composed purely of p-orbitals, armchair tubes and those tubes with lines representing the endpoints of wave vectors accidentally intersecting the K-point (these tubes fulfill $n-m = 3m$) are predicted to be metals $^{68}$. However, Hamada et al. show that in fact armchair tubes are the only metallic class of tubes $^{81}$, all other tubes are either small gap or moderate gap semiconductors. Those tubes without wave vectors coinciding with the K-point are moderate gap semiconductors. Tubes with wave vectors accidentally coinciding with the K-point are found to be small gap semiconductors when the s-character introduced into the $\pi$-band due to the curvature of the graphene sheet is considered. See Table 9 for a summary.

<table>
<thead>
<tr>
<th>Type of tube</th>
<th>bandgap</th>
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</thead>
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<tr>
<td>$n-m = 0$</td>
<td>metal</td>
</tr>
<tr>
<td>$n-m = 3m$</td>
<td>narrow gap</td>
</tr>
<tr>
<td>otherwise</td>
<td>moderate gap</td>
</tr>
</tbody>
</table>

Table 9: Bandgap in dependence of SWNT geometry ($n$, $m$ = integer)
To conclude this summary of electrical properties of SWNTs, it should be noted that for purposes of electron transport SWNTs are a one-dimensional system, since scattering in the direction perpendicular to the tube axis is impossible. Such scattering in the direction perpendicular to the tube axis would correspond to scattering between subbands with different angular kinetic energy within the surface of the tube. However, subbands are spaced much too far apart. Thus, current along the tube axis is carried by a single channel and the system is one-dimensional (the 2 bands crossing at the Fermi-energy have identical angular as well as longitudinal kinetic energy at the point of crossing, \( k = 2\pi/3a \) and thus give rise to a single channel). In an ideal scenario (absence of any scattering mechanisms) electron transport along the tube should be ballistic, and tubes can be viewed as 1-dimensional quantum wires, or electron waveguides\(^85, 86\).

According to the presented theoretical evidence, the ropes should be highly conducting. This expectation was confirmed by measurement of the electrical resistivity \( \rho \) of a single rope by a four point technique. A small piece of raw SWNT felt was clamped to a manipulator. A sharpened platinum tip, previously coated with a 10 nm layer of acrylic polymer adhesive, was then driven a few micrometers into the mat and subsequently pulled out to extract a single rope that thus stretched across between the felt and the Pt tip (see Figure 23). Under an optical microscope (magnification 800×), a current of 0.1 to 1 \( \mu \text{A} \) was run along the rope by connection of opposite poles of a stable dc current source to wires leading to the Pt electrode and the mat. The voltage drop along the rope was then measured between 2 arc grown MWNTs mounted on carbon fibers and positioned into contact on the side of the rope at a measured distance of 5 to 10 \( \mu \text{m} \). The rope was later imaged directly by TEM to determine its diameter.
In three separate experiments with different ropes, linear current voltage curves were observed, with good stability. The calculated resistivity of these ropes ranged from $0.34 \times 10^{-4} \ \Omega \text{cm}$ to $1.0 \times 10^{-4} \ \Omega \text{cm}$. The principal error source here was estimation of the rope diameters from TEM, upper limits were used. The intrinsic axial resistivity $\rho_\parallel$ of an individual SWNT in one of these ropes may be considerably less than the value indicated by this simple four point measurement because the tube-tube resistivity $\rho_\perp$ may be $> 10^4 \times \rho_\parallel$, as it is in graphite, and the ropes measured may not have been long enough to ensure that only $\rho_\parallel$ was being measured. However, the value of $0.34 \times 10^{-4} \ \Omega \text{cm}$ already indicates that these ropes are the most highly conductive carbon fibers known. Their $\rho$ values are about an order of magnitude lower than the lowest $\rho$ yet measured for a catalytically grown MWNT. A sample of eight arc grown MWNTs, annealed at 3120 K to further reduce the number of defects, showed a much wider spread of resistivities than the SWNT ropes studied here, and an average resistivity of $0.826 \ \Omega \text{cm}$. Also measured was the directionally averaged bulk resistivity $<\rho>$ at 300 K for an unoriented piece of felt (1.2 cm by 0.25 cm) by pressing it against a microscope slide with four silver foil contacts (0.4 cm between voltage probes). The resistance was 21 $\Omega$. On the basis of a microscopic thickness determined from the length, width, and measured
mass (150 μg), and an assumed microscopic density of 2 g cm\(^{-3}\), the directionally averaged bulk resistivity has been estimated to be intermediate between C\(_{60}\) and graphite. This estimate, \(3 \times 10^{-3} \, \Omega\,\text{cm}\), is less than two orders of magnitude greater than the single-rope value of \(\rho_{||}\). Likely, the relatively small difference between \(<\rho>\) and \(\rho_{||}\) can be explained by the extreme aspect ratio of the ropes comprising the felt; the length of rope segments is an appreciable fraction of the length between voltage probes such that the number of rope-rope contacts required to ensure continuity between voltage probes is quite low.

Interestingly, the felt measurement yielded a positive temperature derivative \(dp/dT\) near 300 K, a definite sign of metallic behavior. In contrast, an individual MWNT showed thermally activated conductance (negative \(dp/dT\)) \(^90\). To further explore the temperature dependence of electron transport in SWNTs, the resistivity of a single rope was measured as a function of temperature between 4 and 300 K in a He cryostat (see Figure 24). This two-point measurement was scaled by the highest resistivity value obtained for a single rope by four-point measurements at 300 K, \(1.0 \times 10^{-4} \, \Omega\,\text{cm}\).
Rope Resistance

Figure 24: R vs T for a single rope
The temperature dependence of the single-rope resistivity shows three distinct features: (1) The resistivity increases linearly with increasing temperature above a transition temperature $T^*$, well described by a positive linear coefficient of $0.52 \times 10^{-4}$ K$^{-1}$. This agrees very well with the expected metallic behavior for ropes containing a large fraction of armchair tubes. Observation of such evidence of metallic behavior suggests that the effects of defects and disorder are less severe than in previous MWNT studies. (2) At temperatures below $T^*$, an upturn in resistivity is observed. (3) Extrapolating the linear temperature behavior to 0 K, a residual resistivity remains. These 3 regimes will be discussed in the following sections.

Resistance linear in T:
- At first glance, the quasi-linear behavior suggests phonon-limited electron transport in the high temperature limit of a Bloch-Gruneisen picture, in which the weak temperature dependence would be attributed to a relatively small net electron-phonon coupling. The density of states at the Fermi level is so low though, and the corresponding spacing between levels so wide, that the relevant phonons would have to be of energy $\gg kT$ for the temperature range investigated. Thus, inelastic electron phonon scattering can be excluded.

- However, it has been shown that the structure of SWNTs introduces a new scattering mechanism which explains the linear temperature dependence of the resistivity, namely coupling of the conduction electrons to long wavelength torsional shape fluctuations, or twistons. The intrinsic resistivity due to the scattering of electrons by twistons is predicted to be proportional to the absoluted temperature, and the experimentally measured temperature dependence of the resistivity agrees well with the predictions of the twiston theory.

Upturn in resistivity at very low temperatures:
- A simple explanation for the upturn in resistivity at low temperatures is offered by thermal activation of transport across contacts between electrodes and rope. In addition.
only one or few tubes are in direct contact with the electrode, but many tubes carry current. As mentioned in the context of the 4-probe measurement, the conductance through ropes is intrinsically anisotropic though with $\rho_\perp \gg \rho_\parallel$. While $\rho_\perp$ always contributes to the measured resistance, it may dominate at low $T$, and the inter-SWNT transport giving rise to $\rho_\perp$ might also be thermally activated.

- In addition, weak localization might also contribute to an increased resistivity at low temperatures. Langer et al. reported electrical resistance measurements of an individual MWNT. This MWNT's conductance saturates at low temperature, similar to the low $T$ behavior of the SWNTs studied here (although in the MWNT, saturation is only observed at temperatures below 1 K). This behavior is explained in terms of 2-dimensional weak localization: At high temperatures inelastic scatter is dominant, attributed to disorder enhanced electron-electron scatter. Formally, inelastic scatter can be described by the inelastic scattering time $\tau_{\text{in}}$. For MWNTs, $\tau_{\text{in}}$ is inversely proportional to the temperature. As the temperature decreases, $\tau_{\text{in}}$ becomes larger and inelastic scatter is less frequent. This leads to elastic scatter being dominant at low temperatures. For such elastic scatter, the backscattering probability for electrons is enhanced due to constructive interference between the partial electron waves traveling back to their original position along time-reversed paths. The enhanced backscatter probability leads to weak localization and a corresponding decrease in conductance at low temperatures. For the SWNTs studied here, inter SWNT vibrational modes are sufficiently excited at temperatures above $T^\ast$ to destroy phase coherence, and scatter of electrons, for example from twistons, is inelastic. This gives rise to the observed linear increase in resistivity with increasing temperature. However, below $T^\ast$ scattering becomes elastic so that phase coherence leads to an increased backscattering probability, or weak one-dimensional localization and a corresponding increase in resistivity. The observed values of rope diameter and $\rho_\parallel$ suggest that the Thouless criterion for one-dimensional localization will be satisfied for $T < 20-40$ K, assuming that $\rho_\parallel$ is a measure of inelastic scattering and thus controls the cutoff length $L_{\text{Thouless}}$. This is consistent with $T^\ast \sim 35$ K observed for a single rope. As an
aside, the MWNT studied by Langer showed a positive magnetoconductance. Since a magnetic field will contribute to the dephasing of interference effects, localization will be reduced and conductance will be increased in the presence of a magnetic field. Depending on the extent of one-dimensional weak localization in the SWNTs studied here, they should also show a detectable positive magnetoconductance.

- Finally, Peierls pointed out that any one-dimensional metal should break the initial translational symmetry to produce a gap at the Fermi-energy. At some temperature however, thermal effects will be sufficient to diminish this bond distortion and hence eliminate the gap. Since SWNTs are a one-dimensional metal, a Peierls distortion could cause an increase in resistivity at low temperatures. However, Mintmire et al. have predicted that for SWNTs such a distortion should only be stable below 1 K, while transition temperatures $T*$ in single ropes are around 35 K.

Residual resistivity:

- An interesting explanation for the residual resistivity at low temperature offers the quantum resistance of a quantum point contact. A quantum point contact is a restriction connecting 2 macroscopic electrodes, which in size is comparable to the Fermi wavelength and much smaller than the mean free path from impurity scattering. In such a geometry, conduction can be treated as transmission between reservoirs that are maintained at different electrochemical potentials. To explain the associated quantization of conduction, a quantum point contact is viewed as a waveguide, through which only a small integer number of transverse modes can propagate at the Fermi level. Upon leaving the negative macroscopic electrode, the potential in the waveguide drops within a screening length, a few nm, and then stays constant until within a screening length of the positive electrode, and transport of electrons down the waveguide itself is ballistic. Thus, there is no voltage drop along the waveguide itself. The electrical current through a quantum point contact fluctuates in time, but each mode features a time averaged current that is linear in voltage with an apparent resistance of $h/e^2$, or 25 kΩ (the quantum of resistance). The waveguide has a nonzero resistance because reflections occur when a
small number of propagating modes in the waveguide is matched to a larger number of modes in the reservoirs. It has already been pointed out that metallic SWNTs can be expected to behave as a waveguide for electrons. A SWNT connecting 2 macroscopic electrodes should thus behave as a quantum point contact, provided its length is short enough, although with a transmission probability of less than 1 due to the large electrode-rod resistance. The quantized conductance associated with a quantum point contact has indeed been observed for individual SWNTs. Of course, any wave guide channel of a SWNT has a quantum conductance of $e^2/h$, or a resistance of 25 kΩ. The resistance of the single rope extrapolated to 0 K is ~ 1 kΩ. Hence, to interpret the residual resistivity in terms of the quantum resistance of a waveguide requires that the current be carried by 25 tubes out of the more than 100 tubes making up the rope. Truly ballistic transport of electrons down a SWNT should manifest itself in a resistance independent of the length a tube stretches between 2 electrodes as the temperature approaches 0 K.

- Based on the available data, it cannot be completely ruled out that tubes within a rope are not continuous over the entire length of the rope, but rather are segmented, which might give rise to a residual resistivity.
- Finally, physisorbed species like O₂ or H₂O could act as scattering centers and give rise to a residual resistivity.

**Mechanical strength of SWNTs**

The fact that armchair tubes are the only metallic class of tubes makes them very special. But there is even more: Various approaches have been used to gain theoretical insight in the mechanical properties of tubes. Early on it has been predicted using both empirical potentials and local density functional calculations that the elastic properties of SWNTs will depend on tube helicity. For tubes of similar radius, zigzag tubes are expected to be least stiff, while chiral tubes are expected to be of intermediate stiffness. Armchair tubes are predicted to be the stiffest of all tubes. BINGO!
Data related to the strength of nanotubes was first available for MWNTs. The Young's modulus of MWNTs has been estimated by measuring the amplitude of their intrinsic thermal vibrations in a TEM. It was found that the average Young's modulus exceeded the 1 terapascal (TPa) in-plane modulus of single crystal graphite \(^9\). The extraordinary tensile strength of tightly wrapped graphene sheets has also been observed in a process where multi-wall nanocapsules serve as nanoscopic pressure cells for diamond formation \(^{100}\). However, it has also been shown that MWNTs are often highly defective with a local structure similar to turbostratic graphite \(^5\). Such a high defect density can be tolerated in MWNTs since defects can be stabilized by interaction with neighboring layers. This presence of defects will keep MWNTs from reaching their ultimate tensile strength though, and will impact their practical performance. Since for the individual graphene sheets in SWNTs no neighboring layers are available to interact with, defects cannot be stabilized, and a tube would likely close rather than tolerate a defect. One might thus expect SWNTs to be defectfree. On these grounds, SWNTs should be extremely resilient under stress. This resilience is demonstrated in Figure 25, which shows a tube that did not break despite being severely kinked.
Figure 25: Kinked nanotube
That a tube bent beyond its buckling point will assume such a distinct kink shape is part of a more general prediction that nanotubes subject to large deformations will reversibly switch into different morphological patterns, without bond breakage \(^{101}\). Largely distorted configurations due to purely elastic deformations without the presence of atomic defects have also been observed by others in the form of collapsed nanotubes \(^{102}\).

Using an elastic model accounting for central and angular forces for nearest neighbor bonds, the C\(_{500}\) tube with endcaps identical to C\(_{60}\) cut in half was predicted to be about one order of magnitude stiffer than an iridium wire of comparable size \(^{103}\). This translates into a Young's modulus greater than 5 TPa. In agreement with these results, simulations using a many-body potential predict a Young's modulus of 5.5 TPa for SWNTs of 1 nm diameter \(^{101}\). The same work also predicts that carbon nanotubes can be stretched by as much as 40% before breakage occurs. Combination of Young's modulus and elongation at failure gives a tensile strength of 5.5 TPa \(\times 0.4 = 2.2\) TPa for an individual tube of 1 nm diameter.

Considering that the graphite in-plane Young's modulus is only \(Y = 1\) TPa, the Young's modulus \(Y > 5\) TPa presented above for SWNTs seems surprising. At the heart of this apparent discrepancy lies the fact that for very tightly wrapped tubes the graphite shell is squeezed into a smaller area, and is placed along the perimeter of the cylinder, which is optimum for stiffness. This manifests itself in a large modulus, which by definition is per area \(^{104}\). The hollow structure of a nanotube results in especially high rigidity with respect to bending. From a numerical point of view, the dilemma is resolved by noting that in reference \(^{101}\) the elastic properties of a nanotube are modeled by assigning it a shell thickness \(h\) and a Young's modulus \(Y\), avoiding details of the atomic interactions. In order to reproduce the extraordinary bending stiffness of a nanotube just 1 nm in diameter, a narrow shellwidth \(h = 0.66\) Å in combination with an inflated Young's modulus \(Y = 5.5\) TPa is used. These parameters also describe elongation of a tube correctly, however, tension along the tube axis might as well be described by a shell width equal to the
graphite inter-layer spacing ($h = 3.4 \, \text{Å}$) and the graphite in-plane Young's modulus ($Y = 1 \, \text{TPa}$), since $5.5 \times 0.66 = 1 \times 3.4$.

After the preceding discussion it should be clear that a reasonable description of the mechanical behavior of laser generated SWNTs can be obtained using the graphite in-plane Young's modulus of 1 TPa. The tensile strength of a rope can then be estimated by taking a strip of a graphene sheet having a width equal to the circumference of a (10,10) tube, 4.27 nm, multiplying by the van der Waals spacing of graphite, 0.34 nm, and by the graphite in-plane Young's modulus to arrive at an elastic constant of $1.45 \times 10^6 \, \text{N per tube}$. Dividing this by the cross-sectional area occupied per nanotube in a triangular lattice, $2.5 \times 10^{18} \, \text{m}^2$, gives a Young's modulus for such a close packed fiber of (10,10) tubes of 581 GPa. This is not recordbreaking, since carbon fibers with Young's modulus up to 800 GPa are known. The resulting tensile strength of 232 GPa however, calculated using the predicted 40% elongation at failure, is extraordinary (about 150 times the tensile strength of steel).

In order to test the strength of SWNT ropes, centimeter long fibers of largely aligned strands of SWNTs were grown in a setup similar to the "advanced laser-oven-setup". Two opposing, electrically isolated grids were mounted inside a 4 inch diameter quartz tube downstream from the target. Both grids were oriented perpendicular to the flowing argon buffer gas, and separated by 2 centimeters. The grid near the target was biased positive, while the grid further downstream was connected to ground via a resistor. A grounded mesh cylinder surrounding the grid electrodes was used to exclude possible electric fields resulting from electrostatic charges on the insulating quartz tube. After unblocking the lasers, ropes drifting with the inert gas deposited on the first grid. Soon more rope material attached to these to form macroscopic fibers, aligned by the electric field to point towards the downstream grid. Eventually fibers spanned the gap between the 2 grids, establishing an electrical connection between the electrodes. Due to the positive bias applied to the first grid, a current began to flow to the downstream grid, causing a voltage
drop across the resistor connecting the downstream grid to ground. This voltage drop was fed into an analog to digital converter (ADC), allowing to monitor the growth of fibers by following the current flowing from the downstream grid to ground. For lasers q-switched at 10 Hz, the current would start to rise within the first second, and then reach several tens of μA within 10 seconds. By this time numerous fibers visible to the eye would span across the 2 cm gap.

Fibers investigated in the SEM were found to exhibit a remarkable degree of alignment (see Figure 26). They consist of a collection of strands, which appear to have one or a few ropes at their core. The backbone of strands likely is not formed by one continuous rope, but rather by several ropes tied to each other in knots hidden in tangles (see Figure 27) always seen along the length of strands.
Figure 26: Strands of SWNTs, note the alignment
Figure 27: SWNTs tied together in a nanoknot
The tensile strength of these strands was then measured. A commercial carbon fiber (CCF) was used to apply a force oriented perpendicularly to a strand supported by 2 wires. This caused the strand to stretch, while at the same time the CCF bent. The tensile strength of the strand was then obtained from the bend of the CCF at the point the strand snapped.

A fork consisting of 2 thin wire tangs (0.23 mm diameter, 1 cm long) attached to a banana plug was used to collect a fiber by sweeping it through the as-grown material between the 2 grids. Adhering to the wires by van der Waals forces, the fiber would span the gap between the 2 wires in a taught manner. Fibers were then fixed in place by applying a dab of silver paint to the points of contact between the fiber and each tang. Subsequently the fork supporting the fiber was mounted on an XYZ-translation stage on an inverted microscope (Zeiss Axiovert 135 A) such that the fiber was perpendicular to the optic axis of the microscope and both tangs were in the field of view at 80× magnification. The length of the fiber between the tangs $\Delta Y$ was determined with a measuring reticule. An opposing XYZ-translation stage supported a 1 cm long 26 gauge nichrome wire, to which a CCF was attached. The CCF was oriented perpendicular to the fiber and perpendicular to the optic axis of the microscope.

By scanning the edge of the SWNT fiber oriented towards the CCF at 800× magnification, a single strand was located. The CCF was then positioned in a plane just above the strand and translated so that its tip passed the strand by 10 μm. Subsequently, the CCF was lowered to just touch the strand. Contact was indicated by the strand going slightly out of focus (depth of field 1 μm). The Z micrometer position for the CCF at this point is denoted $Z_0$.

Next, the CCF was slowly translated down, keeping the point of contact between the strand and the CCF in focus. The force applied by the CCF increased the tension in the
strand, while the CCF bent. As the tension in the strand exceeded its tensile strength, the strand broke. The Z micrometer position at this time was denoted $Z_l$. Not being held by the strand any longer, the CCF straightened out at this time, and the tip of the CCF suddenly jumped out of focus.

To determine the displacement $\Delta Z$ of the tip of the CCF by the strand at the point the strand broke, the CCF was now moved back into the focus plane, using the Z micrometer. This final Z micrometer position for the CCF was denoted $Z_2$. The displacement of the CCF is then given by

$$\Delta Z = Z_2 - Z_l.$$ 

For small displacements $\Delta Z$, the force $F$ applied by the commercial carbon fiber to the strand is given by

$$F = k \Delta Z,$$

where $k$ is the bending force constant of the CCF. For the determination of $k$, see Appendix 3: "Bending force constants of carbon fibers". The tension $F'$ in the strand due to force $F$ can then be obtained from simple vector addition as

$$F' = F / (2 \sin \theta),$$

where $\theta$ is the out of plane angle acquired by the strand, defined as

$$\theta = \tan^{-1} \left[ 2 \Delta Y / (Z_l - Z_0) \right]$$
The tensile strength $T$ of a strand can then be derived from the tension $F'$ the strand was suffering at the point it broke as follows:

$$T = \frac{F'}{A}$$

where $A$ is the cross-section of the strand. Table 10 lists the tension at breakage and the tensile strength derived from that for 15 different measurements:

<table>
<thead>
<tr>
<th>Number of strands broken</th>
<th>Tension/strand (nN)</th>
<th>Tensile strength (GPa)</th>
</tr>
</thead>
<tbody>
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<td>1</td>
<td>3320</td>
<td>13.28</td>
</tr>
<tr>
<td>1</td>
<td>545</td>
<td>2.18</td>
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<td>220</td>
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<tr>
<td>1</td>
<td>410</td>
<td>1.64</td>
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<tr>
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<td>406</td>
<td>1.624</td>
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<tr>
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<tr>
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<tr>
<td>1</td>
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</table>

Table 10: Tensile strength of strands of SWNTs

The tensile strength was calculated assuming that breakage of a strand corresponds to breakage of a rope containing 100 (10,10) tubes with a cross-section of $2.5 \times 10^{-16}$ m$^2$. The average tensile strength of strands of 2.29 GPa is much lower than the expected intrinsic tensile strength of ropes of SWNTs (A tensile strength of 232 GPa was predicted for a rope!). This must be due to the fact that strands do not have a rope continuous over
their entire length at their center. Previously it has been pointed out that individual ropes seem to be tangled and tied together in knots: Under tension, these knots may come undone simply due to ropes slipping past each other. It is also likely that while in straight sections of a rope tension is oriented along the rope axis, within knots forces are present that are oriented at an angle to the rope axes. Since tubes are strongest in direction of their axis, such forces at an angle to tube walls will cause tubes to break at lower forces. Still the tensile strength of strands is comparable to the tensile strength of high strength steel, which is about 1.5 GPa.

The possibility that simple van der Waals contact between ropes is responsible for the observed tensile strength of strands can be ruled out, as can be shown by considering two ropes in contact for 10 µm of length, assuming that 10 nanotubes from each rope are in van der Waals contact with 4 carbon atoms involved per nanotube per 0.246 nm unit cell. For an estimated van der Waals binding energy of 0.01 eV/atom, the total van der Waals energy over the 10 micron length is $3.25 \times 10^4$ eV. The energy stored in the CCF when the strand snaps is given by $\frac{1}{2} k (\Delta Z)^2$. For the Zoltech CCF having an average displacement of $7.2 \times 10^{-5}$ m this energy is $1.68 \times 10^{11} J = 1.05 \times 10^{8}$ eV or nearly 4 orders of magnitude larger than the estimated van der Waals energy. In summary, the presented measurements seem to confirm the idea that ropes within a strand are tied together in little nanoknots, since strands are not as strong as should be expected if they were supported by a continuous rope at the center, nor can strands be simply held together by van der Waals forces.

Typically the strength of materials suffers from the presence of microcracks. Under stress these cracks lead to failure long before the theoretical limit for the defect-free material has been reached. Part of the theoretical strength can be recovered by laminating materials. The development of macroscopic cracks is suppressed as microcracks do not propagate across layers. In this respect it is interesting to note that a nanotube based fiber is
naturally laminated, since adjacent tubes are only van der Waals bonded to each other. Thus, ultimately, SWNT based fibers are likely to realize a significant fraction of their theoretical strength.
The Bowl Road

In the chapter "Growth mechanism of SWNTs" it was argued that for SWNTs with an open growing edge it is energetically most favorable to have a zero helicity armchair edge, which together with the experimental evidence served to establish the dominance of the (10,10) tube. While apparently the diameter of the tube is locked into place when the cluster contains between 300 and 500 atoms, the question at what stage the edge arranges into the armchair configuration was left unanswered.

It has been pointed out that a (10,10) tube is closed by a $C_{340}$ hemi-fullerene dome with a corannulene-like $C_{20}$ unit serving as the key stone in this dome. The isolated center structure, a pentagon surrounded by 5 hexagons, is a graphene sheet that has been curved due to incorporation of the pentagon. One might expect corannulene-like $C_{20}$ to suffer heavily from 10 dangling bonds. Strikingly though, corannulene-like $C_{20}$ has an edge that allows all 2-coordinated carbon atoms to participate in triple bonds just like 2-coordinated carbon atoms in an armchair edge do! As a direct extension of $C_{20}$, a series of open, curved bowl structures $C_{30}$, $C_{40}$, and $C_{50}$ can be devised with only nonadjacent pentagons, their pentagons and hexagons arranged so that the periphery of the cluster is in the armchair configuration and all 2-coordinated atoms are part of triply-bonded pairs (see Figure 28). The final element in this series of geometries is $C_{60}$-Buckminsterfullerene (in the following referred to simply as $C_{60}$).
Figure 28: Open, curved bowls with armchair edges

A series of open, curved bowls $C_{20}$, $C_{30}$, $C_{40}$, and $C_{50}$ can be devised with all 2-coordinated edge-atoms part of triply-bonded pairs. The concluding element in this series of geometries is $C_{60}$. 
Clusters of carbon are found in vapor at equilibrium with solid graphite even at temperatures of several thousand degree Celsius \(^{107}\). For small clusters, linear chains present the most stable geometry \(^{108}\). These chains grow longer by addition of small carbon radicals like \(\text{C}_2\) and \(\text{C}_3\). Slightly bigger clusters containing more than 10 carbon atoms arrange into rings \(^{109}\). As clusters continue to grow, however, more compact geometries start to outperform low-dimensional structures: Coupled-cluster calculations predict the fullerene and the bowl to be close contenders for the lowest energy structure of \(\text{C}_{20}\) \(^{110}, 111\). A quantum Monte Carlo approach shows \(\text{C}_{20}\)-bowl to be lower in energy than either the fullerene or an alternative ring structure \(^{112}\). The relative order of stability for different geometries at the formation temperature of fullerenes will also depend on entropic factors. Due to vibrational entropy, the ring geometry will experience the largest stabilization, while the bowl will experience somewhat less stabilization and the fullerene has the least to gain. All things considered is \(\text{C}_{20}\)-bowl between approximately 700 K and 1500 K more stable than \(\text{C}_{20}\)-fullerene and still more stable than \(\text{C}_{20}\)-ring \(^{110}\).

The efficiency with which armchair tubes form suggests that carbon clusters tend to anneal towards armchair geometries even in early stages of condensation. Bearing in mind the intimate connection between tube growth and fullerene growth, and the astonishing similarity between corannulene-like \(\text{C}_{30}\) and armchair tubes, they might even do so well before they get ready to close into a fullerene, that is, well before they contain 60 carbon atoms: Clusters rearrange into bowl-shaped fullerene-precursors with their open edge energy reduced by formation of triple bonds between 2-coordinated carbon atoms, which are thermodynamically favored over low-dimensional structures. Such precursors are then predetermined to grow into \(\text{C}_{60}\) in a pure carbon environment.

For larger clusters are the closed fullerene structures actually more stable than bowl-shaped structures, even before they have grown to contain 60 carbon atoms. \(\text{C}_{50}\)-fullerene for example is calculated to be more stable than \(\text{C}_{50}\) bowl by 8 eV \(^{113}\). However, closure of such bowl-shaped fullerene-precursors into a fullerene has to rely on accident to
overcome the barrier separating the two: The first step in the transformation of $C_{50}$-bowl into $C_{50}$-fullerene is a 1.2 carbon shift to convert one of the edge hexagons into a pentagon with a dangling carbon atom. The pentagon product is about 2 eV uphill from the armchair $C_{50}$-bowl. Now a neighboring edge hexagon has to rearrange during the lifetime of this dangling carbon atom via the same 1.2 carbon shift to produce another dangling carbon atom, which can then bond with the first dangling carbon atom. Bond formation creates a new hexagon, while the 1.2 carbon shifts transformed two of the original hexagons into pentagons. From here on it’s straightforward to complete closure, sequential 1.2 carbon shifts in the remaining hexagons of the original armchair edge introduce the required number of pentagons to close $C_{50}$-bowl into $C_{50}$-fullerene. Critical in this mechanism is the requirement for two simultaneous 1.2 carbon shifts on neighboring hexagons of the armchair edge to start closure of $C_{50}$-bowl. The bowl supporting two carbon sticks is a target in phase space that is very hard to find of course. Being offered feedstock constantly, clusters in all likelihood incorporate more carbon on their open edge before accident provides a chance to close, making the conversion of bowls into fullerenes an extremely rare event. Once small carbon radicals have assembled into bowls annealing towards armchair structures, kinetics directs growth towards $C_{60}$, even though there are closed fullerenes containing less than 60 carbon atoms along the way that are thermodynamically more stable than the proposed intermediates.

In summary, under conditions favoring the formation of fullerenes in high yield, coalescence of the condensing vapor results in small linear carbon chains and rings, a large fraction of which eventually assemble bowl shaped graphene sheets, annealing towards armchair geometry. These intermediates continue to grow directly into $C_{60}$, since for clusters containing less than 60 carbon atoms no straightforward path leading to closed structures is available. On the other hand, they rarely overshoot since they are predetermined from early on to grow into $C_{60}$. This predetermination to grow into $C_{60}$ is important considering that there is little reason for fullerenes larger than $C_{60}$ to get smaller since they have a higher binding energy per atom than $C_{60}$. It is important to
emphasize the role assigned to bowl-shaped intermediates under conditions of highly
efficient fullerene formation, when much of the carbon feedstock is converted into
fullerenes, $C_{60}$ in particular: Bowl-shaped intermediates are formed and converted into
$C_{60}$ at a high rate, most of the carbon heading towards $C_{60}$ passing through them. This
does not require that they be present in large amounts, on the contrary, their concentration
is likely to be low since they react away fast.

In agreement with experiment, the model presented here predicts $C_{60}$ to be only slightly
more abundant than other fullerenes if the concentration of reactants is low, as could be
caused by a rapidly expanding plume due to a low inert gas pressure for example. First of
all, clusters will cool faster as the plume expands more rapidly. There will then be very
little annealing and most clusters will either have grown very large before they
incorporate enough pentagons to close, forming giant fullerenes, or will never close. The
few cluster that do incorporate pentagons in time to form fullerene-precurors like $C_{50}$-
bowl now have time to sample phasesspace between infrequent collisions with feedstock.
Most likely they will then close into fullerenes smaller than $C_{60}$.$^{25}$

One last issue will have to be addressed: Initially, small clusters grow as a result of
collisions wit1 even smaller feedstock. As graphene sheets grow bigger though, much of
the initially abundant small species like $C_{2}$ and $C_{3}$ will have been consumed. It appears
however that closure of fullerene-precurors like $C_{50}$ into $C_{60}$ requires the presence of
small feedstock even during the final steps of fullerene growth. This problem can be
avoided by allowing a growing graphene sheet to add only part of a cluster encountered in
a collision.$^{115}$ This way $C_{50}$ can close into $C_{60}$ even if it collides with a cluster containing
more than the needed additional 10 carbon atoms, the incorporation of more carbon
driven by the fact that $C_{60}$ has a higher binding energy per atom than the feedstock. The
remainder of the now smaller collision partner can serve as further feedstock.
An earlier model explaining the facile growth of $C_{60}$ and other fullerenes is the Isolated Pentagon Road. At its core stands the idea that a cluster has to balance the energy cost of curving the graphene sheet and the energy cost of having dangling bonds associated with its open edge. The first factor will favor a flat graphene sheet to reduce strain energy, while the second factor will favor a tightly wound sheet with only a minimum number of dangling bonds. As a result, clusters include pentagons in order to reduce the number of dangling bonds, but avoid adjacent pentagons, which would cause excessive stress. Under annealing conditions, the bulk of the carbon clusters reaches $C_{60}$, which is the first cluster to reduce the number of dangling bonds to zero, while having only nonadjacent pentagons.

Having established that the dangling bond energy does not simply scale with the length along the perimeter, but depends critically on the detailed geometry of the open edge, it is time to review the Isolated Pentagon Road. It is true that incorporation of a pentagon will always introduce strain relative to the alternative introduction of a hexagon. However, introduction of a pentagon does not necessarily reduce the number of dangling bonds, as was assumed in the Isolated Pentagon Road: For example, adding one carbon atom to $C_{50}$-bowl to form the seventh pentagon produces three dangling bonds. In general, adding pentagons cannot be done without introducing a portion of zigzag edge, with an energy cost of about 0.8 eV per dangling bond associated with a zig atom. For clusters to continue growth along their path leading to fullerene-precurors ready to close into $C_{60}$, such locally non optimum structures need to be temporarily frozen in at the edge until enough carbon has come in, and enough pentagons are included, to arrive at favorable triply-bonded intermediates and finally bridge the gap. Therefore, there is always a barrier to closure of open bowls into fullerenes. Fortunately, this barrier is routinely overcome under fullerene growth conditions since the locally non optimum structures are sufficiently long-lived. In the presence of a SWNT catalyst however, these locally non optimum structures continually fall victim to the scooter, whose role it is to anneal away any locally non optimum structures. A sufficient number of fullerene-precurors is then
prevented from closing to transform more than 70% of the condensing carbon vapor into SWNTs.
Appendices

Appendix 1: Plume expansion

An estimate of the time required for the expanding plume to cool below the annealing temperature of carbon clusters can be obtained by assuming that the front of the plume moves at the speed of sound and expansion of the plume can be treated as adiabatic. Assuming adiabatic conditions is equivalent to requiring that the moving front of the plume completely sweep the helium atmosphere out of the volume to be occupied by the plume so that there be no thermalization of material contained in the plume by helium gas. Since the initial volume of the plume will be negligible compared to its volume after cooling below the annealing temperature of carbon clusters, the volume $V$ of the plume after cooling by $\Delta T$ due to expansion against a gas of pressure $p$ is given by

$$V = - \frac{\Delta T \ C_v}{p} \quad (1)$$

where $C_v$ is the heat capacity of the material contained in the plume. Restricting material vaporized in an area $A$ on the surface of the target to expand only perpendicularly to the surface, the time $t$ it takes the plume to cool by $\Delta T$ is then given by

$$t = \frac{V}{A \nu} = - \frac{\Delta T \ C_v}{p \ A \nu} \quad (2)$$

where $\nu$ is the speed of sound in the inert gas atmosphere. The rotational and vibrational temperatures in carbon plasmas generated by laser ablation of graphite using comparable laser flux have been determined from $C_2$ molecular spectra to be 5000 K and 6000 K, respectively. The electronic temperature is likely to be even higher. An estimate for
the initial plasma temperature of 6000 K thus seems reasonable. Since annealing slows dramatically below 1400 K, the plasma must have cooled by $\Delta T = 4600$ K before annealing effectively comes to a stop. The heat capacity of the material contained in the plume $C_v$ can be calculated by multiplying an average molar heat capacity $C_{vm}$ by the amount of material vaporized by one laser shot. Laser vaporization will initially produce very small carbon radicals. For $C_2$, $C_{pm} = 43.21$ J K$^{-1}$ mol$^{-1}$ and $C_{vm} = 34.90$ J K$^{-1}$ mol$^{-1}$ at standard temperature. However, at the high temperatures early on in the expansion, contributions from vibrational modes as well as electronic excitations will cause the heat capacity to be substantially higher, say $C_{vm} = 50$ J K$^{-1}$ mol$^{-1}$ for $C_2$. Thus, the heat capacity per carbon atom is $C_{vm} = 25$ J K$^{-1}$ mol$^{-1}$ at the beginning of the expansion. While the electronic and vibrational contributions to the heat capacity will drop drastically while the plume cools, the continuous formation of bonds will effectively keep the heat capacity at a high level during much of the expansion. Thus, $C_{vm} = 25$ J K$^{-1}$ mol$^{-1}$ is used as heat capacity over the entire temperature range. At a laser repetition rate of 10 Hz, a vaporization rate of 30 mg carbon per hour translates into $6.94 \times 10^{-8}$ mol carbon vaporized by one laser pulse. The heat capacity of the material contained in the plume is then $C_v = 1.74 \times 10^{-6}$ J K$^{-1}$. The vaporization rate of 30 mg carbon per hour is obtained by focusing a laser pulse of 300 mJ onto an area $A = 0.2$ cm$^2$. A typical value for the pressure of the confining helium is $p = 500$ torr, in which the speed of sound is $v = 10^5$ cm s$^{-1}$ at 300 K. According to equation (2), under these conditions the temperature of the plume has dropped to below the annealing temperature of carbon clusters after 6 microseconds. In reality, radiative cooling as well as thermal conduction and convective cooling will play a role since much of the vaporized material follows the shockfront closely, making the cooldown nonadiabatic. In addition, the expansion will be supersonic initially. As a result, cooldown of the plume will be faster, on the order of a microsecond. Plumes resulting from IR laser ablation of graphite have been analyzed and time resolved emission spectrograms were obtained. Under helium atmosphere, the 516.5 nm
emission of $C_2$ could be observed for $950 \pm 100$ ns. This agrees well with the above estimate of the time required for the cooldown of a laser generated plume.
Appendix 2: Parameters in fullerene production

The following Table summarizes the effects of several parameters on the fullerene yield in the laser-oven-setup with a one inch diameter quartz tube:

<table>
<thead>
<tr>
<th>Pressure (torr)</th>
<th>Gas flow (sccm)</th>
<th>Focus (cm,cn)</th>
<th>Mass vaporized (mg)</th>
<th>Mass collected (mg)</th>
<th>Collection efficiency (%)</th>
<th>Yield (%)</th>
<th>Laser flux (mJ/mm²)</th>
</tr>
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<tr>
<td>1</td>
<td>250</td>
<td>20</td>
<td>200.70</td>
<td>18.6</td>
<td>4.2</td>
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<td>20</td>
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<td>200.52</td>
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<td>28</td>
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<tr>
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<td>5</td>
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<tr>
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<tr>
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<tr>
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<td>25.0</td>
<td>16.9</td>
<td>0.68</td>
<td>44</td>
</tr>
</tbody>
</table>

Table 11: Parameters in fullerene production

\[1\] The focus is described by 2 numbers: focus length of the lens, distance between the lens and the face of the target.

\[\text{ii}\] Collection efficiency is defined as the mass deposited on the water cooled collector divided by the mass loss of the target due to laser irradiation.

\[\text{iii}\] Yield is defined as the weight of fullerenes extracted from the collected soot divided by the weight of the collected soot.
Appendix 3: Laser induced plume heating

To estimate the amount of energy coupled into the plume by the second laser via absorption by small radicals, the following assumes that all material contained in the plume is present as C$_2$ radicals, with an absorption cross-section of $\alpha = 10^{-24}$ m$^2$ per C$_2$. Under dual laser conditions, a vaporization rate of 140 mg carbon per hour is not atypical if lasers run at 30 Hz. One plume then contains $1.1 \times 10^{-7}$ mol carbon, equivalent to $6.62 \times 10^{16}$ carbon atoms or $3.31 \times 10^{16}$ C$_2$ radicals. (140 mg is really the mass contained in the plume after both laser pulses. However, most of the material vaporized by the second laser will be vaporized early during the second laser pulse. It is fair then to consider a plume containing 140 mg carbon interacting with the second laser pulse.)

Since the speed of sound in argon at 1200°C is 720 m s$^{-1}$, the original plume has expanded out to $l = 28$ µm from the face of the target by the time the second laser pulse arrives 40 ns after the first laser pulse. For beams of 5 mm diameter, the volume occupied by the plume is then $5.66 \times 10^{-10}$ m$^3$. If all C$_2$ radicals were uniformly distributed throughout this volume, the C$_2$ concentration would be $c = 5.86 \times 10^{25}$ m$^{-3}$.

According to the Beer-Lambert law, a fraction $(1-T)$ of the second laser pulse will be absorbed by the plume, given by

$$1 - T = 1 - \frac{I_l}{I_0} = 1 - e^{-\alpha cl}$$

where $T$ is the transmittance, $I_0$ is the incident intensity, and $I_l$ is the intensity of the beam after passing the plume. For the example under consideration, 0.169% of the incident light, or $5.9045 \times 10^{-3}$ J out of 0.35 J will be absorbed by the plume. Since the heat capacity of the plume will be roughly $2.7 \times 10^{-6}$ J K$^{-1}$, this energy is sufficient to raise the temperature of the plume by 218 K.
Appendix 4: SWNTs from preformed metal particles

Iron as catalyst produced an exceedingly low yield of SWNTs in the laser-oven-setup. However, as has been mentioned before, Iijima found that in the presence of methane in the arc chamber iron does catalyze the formation of SWNTs. The helicity of a single tube from a sample of SWNTs obtained in the arc with iron as catalyst was investigated by electron diffraction. Interestingly, this tube turned out to have (18,2) geometry, meaning that it came close to being zigzag. The large number of dangling bonds the open edge of such a tubelet would have is in striking contrast to expectation if tubes were nucleated by the scooper mechanism. If alternatively tubes were nucleated from a metal particle however, at no point during nucleation would tubelets have an open edge. A zigzag edge might actually be favorable, since the bonds extending from the zigzag edge will be chemisorbed most strongly to the attached metal particle. The presence of nanometer sized metal particles in the arc that either form early or never vaporize completely is certainly conceivable. Likely, the methane serves as a feedstock that is catalytically decomposed by the iron particles.

That SWNTs can indeed grow from preformed metal particles has been shown: Isolated SWNTs were grown by disproportionation of carbon monoxide at 1200°C, catalyzed by molybdenum particles a few nanometers in size. Tube diameters, ranging from 1 to 5 nm, closely correlated with the size of the catalytic particles found attached to tube-ends.

The nucleation of SWNTs from a preformed metal particle is a consequence of the dominant role surface energy plays for a nanoscale particle. A metal particle only a few nm in diameter contains a very high percentage of surface atoms, creating a tremendous surface energy problem on a per atom basis. An excess of carbon, for example due to disproportionation of CO on the particles surface, can help to solve this problem by assembling a graphene cap on the particle surface, with its edges strongly chemisorbed to
the metal. Since the basal plane of graphite has an extremely low surface energy (10 to 20
times smaller than most metals), the total surface energy diminishes. Incoming new
carbon will add to such a cap, until it has grown into a hemisphere. At this point, new
carbon will likely insert between the edge of the cap and the metal particle to lift the cap
off the particle, forming a short tube. The alternative, continued growth of the cap around
the particle, requires the incorporation of additional pentagons, while the formation of a
tube allows all additional carbon to take the more favorable form of hexagons. According
to this model, the diameter distribution of SWNTs is determined by the size distribution
of catalytic particles, in marked difference to the scooter model.

The innermost tubes of MWNTs can have diameters as small as 3 nm. However, the
disproportionation of CO on preformed particles produces single-wall fullerene
nanotubes with diameters up to 5 nm. At first it seems likely that additional caps should
nucleate underneath the first cap and grow into tubes of smaller diameter, forming a
MWNT with an outer diameter of 5 nm. The key to this question again may lie in the
crucial role surface energy plays for particles in the nanometer size range. In order to
nucleate additional caps underneath the first cap, feedstock would have to migrate
through the interior of the catalytic particle to the place where additional caps are to be
nucleated. However, a nanometer sized metal particle with carbon dissolved throughout
its bulk can lower its surface energy dramatically by excluding the carbon from its interior
to form a graphene sheet conforming to its outside. This effect might not allow carbon to
migrate into the interior of such small particles in the first place. Rather, feedstock will
only sample the surface of the particle and get completely included in the one tube
initially nucleated. To nucleate this first tube, no migration of carbon through the metal
particle was necessary. For larger metal particles, as encountered in the catalytic growth
of MWNTs, the relative importance of surface effects diminishes, and it becomes viable
for carbon to migrate into the interior of the catalytic particle, followed by nucleation of
additional caps underneath the original cap.
Catalysts were prepared by mixing bis(acetylacetonato)dioxomolybdenum with fumed alumina nanoparticles (1:10 by weight) suspended in methanol. The solvent was removed in a rotovap overnight, and the resulting powder was heated in a furnace at 200°C for 12 hours. The material was then pulverized into a fine powder by grinding and passing through a fine mesh sieve (80 mesh). The process leaves the molybdenum probably as an oxide. That this preparation produced particles with a size distribution more strongly skewed towards small sizes than is typical in other catalyst preparations was certainly helpful to the formation of SWNTs. Possibly the actual catalytic particles 1 to 5 nm in diameter form only upon heating the system to its 1200°C operating temperature: In this scenario, the volatile MoO₃ would sublime from its support and subsequently be reduced in the gas phase by CO. This would lead to the condensation of small Mo particles of the right size to catalyze the growth of SWNTs. Metal particles large enough to nucleate MWNTs were also present, but usually enclosed in onions. No MWNTs may have grown since the rate with which CO disproportionates on the surface is independent of particle diameter, while the time it takes new carbon to migrate to an initially formed cap increases. This may lead to the formation of several caps on large metal particles, which form the first layer of an onion and never lift off the particle.
Appendix 5: Young's modulus of carbon fibers

A "Sigri" and a "Zoltech" commercial carbon fiber (CCF) were used to measure the tensile strength of SWNT strands. The Young's modulus of these CCFs was determined by measuring their respective Euler buckling force. Fibers were mounted aligned with the translation direction of a motorized drive. Fibers were then driven under computer control into the platform of a balance capable of measuring weight with a precision of 0.1 mg. The increasing force applied by the fiber is sensed by the balance and displayed as increasing mass readings $m$. As the applied force reaches the buckling force of the fiber however, the fiber buckles, and the force applied to the balance remains constant despite further translation of the motorized stage. Thus, the mass reading of the balance levels off at some value $M$. The Young's modulus $Y$ can then be obtained from

$$F = Mg = \left( \pi^2 Y r^4 \right) / \left[ 4 (0.7L)^2 \right],$$

where $g$ is the gravitational constant, $r$ is the radius of the CCF, and $L$ is the unsupported length of the CCF. The factor 0.7 arises from the boundary condition on the fiber: On the translator side, the fiber was attached to a piece of 26 gauge wire by a dab of silver paint constraining its slope, while on its other side the fiber was free to pivot about the point of contact with the platform. Radii $r$ of the 2 fibers were obtained from SEM micrographs. Lengths $L$ were determined in a high powered optical microscope using a precision XYZ-translation stage. The Young's modulus $Y$ of the CCF yields then the bending force constant $k$ according to

$$k = \left( 3 \pi Y r^4 \right) / \left( 4 L^3 \right),$$

The following Table specifies the relevant parameters for the CCFs used:
<table>
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<th></th>
<th>$r$ (µm)</th>
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<th>$Y$ (GPa)</th>
<th>$k$ (nN/µm)</th>
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<td>11.9</td>
<td>219</td>
<td>6.503</td>
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Table 12: Parameters of commercial carbon fibers
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