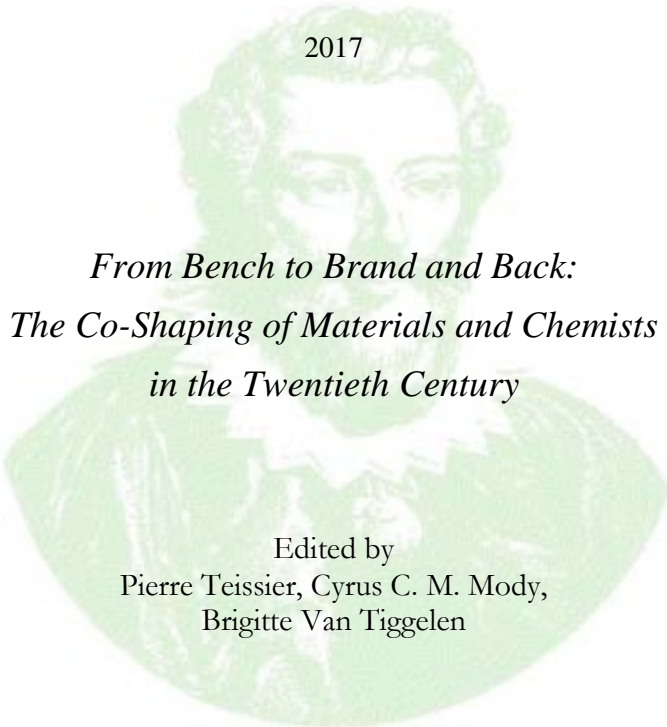# CAHIERS
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From Bench to Brand and Back:
The Co-Shaping of Materials and Chemists
in the Twentieth Century

Edited by
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Point and Line to Plane:
The Ontography of Carbon Nanomaterials

Sacha Loeve[*]

Abstract

The carbons known today as fullerenes, nanotubes, and graphene were all observed or theorized well before becoming emblematic nanomaterials. However, by the 1990s, their mode of existence was shifted from bench or brand objects to technoscientific objects. After focusing on the separate life-stories of these carbons, this chapter recounts how, by eventually interweaving their trajectories and mutually referring to each other, these objects have reborn as a family of low-dimensional nanocarbons unfurling a space of indefinite technological possibilities saturated by promises of radical novelty: the "nanoworld". The co-shaping of nanoworld and nanocarbons is reminiscent of that of the three basic figures composing the world of painting according to Kandinsky: point, line, and plane.

Keywords: carbon, nanotubes, materials chemistry, fullerene, graphene, modes of existence, nanomaterials, nanotechnology, objects, technoscience.

Résumé

Les carbones aujourd'hui connus sous le nom de fullerènes, de nanotubes et de graphène furent tous observés et théorisés bien avant de devenir des nanomatériaux emblématiques, mais au cours des années 1990 ils changent de mode d'existence et passent du statut d'objets scientifiques ou de produits commerciaux à celui d'objets technoscientifiques. En partant des récits de genèse de chacun de ces carbones, ce chapitre raconte comment ces objets, en finissant par entremêler leurs trajectoires et à s'impliquer mutuellement, ont contribué à déployer un espace de possibilités technologiques indéfinies saturé de promesses de nouveauté radicale, le « nanomonde ». La co-constitution du nanomonde et des nanocarbones n'est pas sans évoquer celle des trois figures de base composant le monde de la peinture selon Kandinsky : le point, la ligne et le plan.

Mots-clés : carbone, nanotubes de carbone, chimie des matériaux, fullerène, graphène, modes d'existence, nanomatériaux, nanotechnologies, objets, technoscience.

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T HE NANOSCALE science and technology funding initiatives launched in the 2000s were supported by grand narratives and slogans such as "there's plenty of room at the bottom" or "shaping the world atom by atom" (IWGN, 1999). After the conquest of space, here is the conquest of the "nanoworld". Populated with objects the size of few billionth of a meter in principle inaccessible to our senses, a distant world becomes a land of promises.

In this dizzying world, carbon is king. Fullerenes, nanotubes and graphene (figure 1) are the star materials of nanotechnologies, the stuff their dreams are made of. These all-carbon molecules with iconic shapes have the power to attract thousands of researchers and millions of dollars and to dangle miraculous solutions to all kinds of engineering problems from health to environment and from electronics to mechanics (Pugno, 2006).
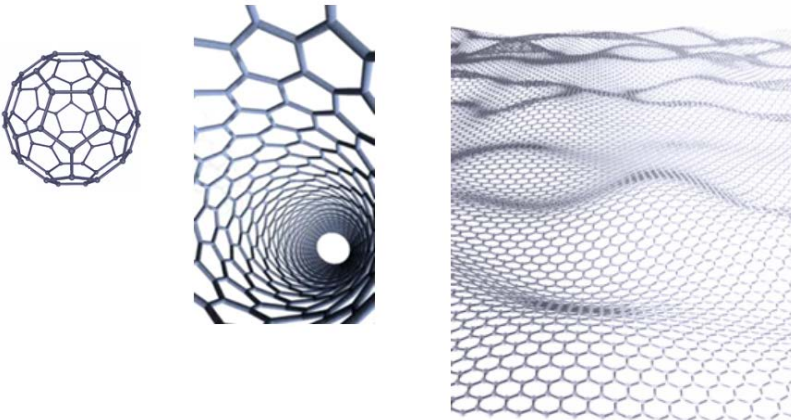
Figure 1 - Point, line and plan of nanocarbons
(Source: picture processed by the author)

But where do these nanocarbons come from? One often reads that carbon nanotubes popped up in 1991 under the electron microscope of Sumio Iijima, physicist of NEC corporation labs at Tsukuba, Japan. His short paper, "Helical microtubules of graphitic carbon" (Iijima, 1991), cited more than 40.000 times, is considered the dawn of a new era, a decisive

first step into the nanoworld.[1] However, nanotubes have been repeatedly characterized (and forgotten) since the 19th century under the name of carbon filaments. The isolation of graphene tells a similar story. While it is generally attributed to Andre Geim and Konstantin Novoselov in 2004, graphene was known as an "academic material" since the mid 20th century. As to fullerene, Harold Kroto, Richard Smalley, and their colleagues synthesized it incidentally in 1985 without knowing that spherical carbon was an object of speculation and chemical reverie for a long time. Moreover, generations of scientists and engineers have inventoried and exploited the characteristics, properties, powers, and behaviors of carbon in all its various forms for centuries (Walker, 1962; Bensaude Vincent & Loeve, forthcoming). Have these marvelous materials simply been revealed by new powerful scientific instruments like scanning probe or electron microscopes or forged by skilled molecular architects? In short, are they discoveries or inventions?

This chapter argues that carbon nanomaterials are the product of a shift in the pattern of existential relations or "modes of existence" that defines them as objects that matter. This notion of "modes of existence" belongs traditionally to the philosophical field of ontology. This field aims at explaining change by what persists through time so that we can hold true beliefs about the world. It usually considers that there is *first*, being (substance, reality, nature, or whatever) and, *only then*, modalization of being, i.e. different ways of saying something about the same existing thing. For instance, for Aristotle I can speak of the same substance according to the category of quality, quantity, locus, relation, etc. I can even vary the degree of existence of that thing from the potential to the actual, but without ever going so far as to change the *being* of this thing, which is assigned to a well-defined identity. So in classical ontology the notion of "modes of existence" is usually taken in a weak sense. It refers to modifications of dictum, not of being.

Here the notion of "modes of existence" is taken in a strong sense along the lines of French philosopher of art Etienne Souriau (1943), who advocated a "muti-realism*",* which has recently been taken over by Bruno Latour (2010). Under this usage the modality attributes another way of being to that which it modifies. Carbon can be apprehended both as a chemical element, as a range of materials, of fossil fuels, as a tool for measuring

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[1] It is in the top ten percent of most-cited science papers (Ho, 2013) and the first most-cited paper for all of materials science. Ironically, those who contest this attribution are quoting the paper and thus contribute to enhance its citation score even more.

our ecological impact ("carbon footprint"), etc. Its multiplicity of modes is nicely suggested by the chemical concept of "allotropy" ("different ways"), but it goes well beyond that of different chemical objects. Each mode typifies a different ontology for carbon, a different way of being in connection with writing (*graphein* in Greek, from which the word "graphite" is formed), a different way for carbon to write itself (through us) (Loeve & Bensaude Vincent, 2017). So instead of ontology this perspective lends itself better to what can be called "ontography" (Lynch, 2013).

Between biography and ontology, ontography sets into narratives the modes of existence of singular things by focusing on the various inscriptions they afford to our material and symbolic practices. So for nanocarbons: they afforded a language of graphemes, surfaces of inscription, geometric structures, operations, and schemes that enabled multiple deterritorializations between bench and brand.

The first three parts retrace the separate life-stories of the turbulent carbon filaments, the academic graphene, and the speculative carbon balloon. The final three parts recount their nano-renaissance in a world of low dimensions: 0D fullerene, 1D nanotubes, and 2D graphene. The conclusion draws an analogy between them and the three basic figures composing the world of painting according to Kandinsky (1929): point, line, and plane.

Doomed to Oblivion: Carbon Filaments

In 1826, Dr. Hugh Colquhoun (1826, p. 2) writes an enthusiastic notice introducing the discovery of "several highly interesting states of aggregation of carbon, one of which is not only of a very singular structure, but also an entirely new form".

The action takes place in the castle of Crossbasket, Blantyre, near Glasgow. In the temporary absence of its landlord, the chemist Charles Macintosh – already famous at that time for his invention of the waterproof fabric – Colquhoun was in charge of superintending the implementation of a new "Macintosh process" for steel-making in a pilot plant apparatus.[2] The process consisted in bringing molten iron to react at high-temperature with a hydrocarbon gas in an airtight pressurized earthen vessel. When the gas is in excess a carbonaceous deposit forms. In this deposit Colquhoun found "capillary threads of carbon", "a mineral hair", whose "single lock seemed to contain thousands of thin filaments" that, "in thickness […] are as delicate as the filaments of the lightest spider-web" (p. 3). After a series of tests, Colquhoun concluded that he was therefore facing a stable and entire-

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[2] English Patent n°5173 (1825).

ly new form of "pure metallic carbon" apart from graphite and diamond. But the story felt short because Macintosh was less happy with steel-making than with its famous raincoat. As the process involved too high temperatures for the state-of-art brickworks it could not be scaled-up. It was quickly abandoned, and the carbonaceous filaments forgotten.

However, carbon filaments resurfaced in two different and independent contexts. First, in the course of bench experiments on "*azotocarbures*" (nitrocarbons), Alsatian chemist Paul Schützenberger, director of the École municipale de physique et de chimie de la ville de Paris and his son Léon, a chemical engineer graduated from the same school, observed "certain facts worthy of interest that pertain to the chemical history of carbon" (Schützenberger & Schützenberger, 1890, p. 774). To achieve full decomposition of cyanogene (N≡C−C≡N), they used a refractory vessel made of almost pure carbon (*charbon de cornue*) powdered with cryolite, a powerful dissolvent. The resulting carbon clogged the tube in a blackish felting presenting long thin filaments. Rubbed onto a sheet of paper, the substance leaves a dark trace reminiscent of "plumbago" (i.e. pencil lead: graphite). But which form of graphite was this "cyanogene coal"? Its oxidation products did not match with any graphite forms identified in the literature. So they cautiously concluded: "the filamentous carbon formed by the pyrolytic decomposition of cyanogene in the presence of cryolitic vapours constitutes a particular variety of carbon, neighbouring but not identical to electric graphite" (p. 777). But if the bench experiments on nitrocarbons were connected to the Schützenbergers' views on organic pigments and artificial cellulose, filamentous carbon was not. Presenting no commercial value in a school and at a time when applications prevailed, the matter ends there.

Carbon filaments reappeared later on in coke ovens. A communication by two industrialists, Constant and Henri Pélabon (1903, p. 706-709), read at the Académie des sciences de Paris by Henri Moissan reports the meticulous observation of "certain deposits with a threadlike appearance and constituting, through the entanglement of their wires, a genuine wool of carbon". This "filamentary carbon" (*carbone filiforme*) forms in the part of the oven exposed most directly to the highest temperatures. It is "generally cylindrical", sometimes with "very thin and tight packages of wires that seem to have arisen in some points of other wires of larger diameter" and "some wires that seem formed of a succession of rings". Their length varies from 5 to 8 centimeters and their thickness between 1 and 15 microns. For the two industrialists the formation of such filiform carbon is undesirable because it is a sign that "the pace of the oven is pushed too far".

Although the Pelabon's report quotes the Schützenbergers' report, neither of them refer to the carbon filaments that Thomas A. Edison was

exploiting with relative success in his incandescent light bulbs. A surprising silence since Edison's invention had famously lighted the Paris World's Fair in 1889. Carbon filaments were selected by Edison at the end of an extensive research program where he spent $40,000 testing 6,000 natural substances over the world before choosing a naturally fibrous organic material containing a large amount of cellulose, bamboo. In 1879, Edison filed a patent describing the processes for obtaining "metallized" carbon filaments by "flash carbonization" of bamboo, i.e., by means of the electric arc previously used for illumination in the first street lamps. "Metallization" also involved repeated electric arc treatment to get very pure ("metallic") carbon. Consisting of twists of several wires measuring about ten microns in diameter, these carbon filaments were featured in the first brand of "Ediswan" light bulbs commercialized in the 1880s and were also used in street lamps.

Thus, at the turn of the 20th century carbon filaments lived two parallel lives in two different technical systems. In coal and steel-making, where they could occasionally be transferred to the chemist's bench, their formation was undesirable, a sign that something went wrong. In early lightbulbs they had a luminous and widely public "brand" existence (Ediswan, General Electric, Shelby…). Electric light was the star of the celebrations of technical progress. But their success was ephemeral. During the interwar period they were supplanted by tungsten on the ground that overheated carbon is sublimed and blackens the bulb after thirty hours of use.

Carbon filaments fell into oblivion for a few decades before being recalled on stage thanks to Transmission Electron Microscope. TEM brought key information about their genesis not only because it is a powerful instrument (TEM provides rather static information) but because carbons bear the traces of their forming events (Rouzaud *et al.*, 2015). However, using TEM did not change the mode of existence of the filaments: it provided knowledge about their conditions of formation so as to *avoid* it. In the 1950s British ceramic chemists studying the wear of blast-furnace brickworks reported TEM observations of helical carbon "vermicules" and pointed out the catalytic origin of this "unusual form of carbon" (Davis *et al.*, 1953). The vermicules' growth was catalyzed by iron particles and a clear relationship was established between the initial particles' distribution and the growth and form of the filaments. A single metallic "speck" gives rise to a single carbon thread measuring as little as 10 nanometers, while a collection of "points" gives rise to many twisted threads forming a bigger "rope" of several microns so tough that it can penetrate deeply in the brick and provoke its rupture. The metal particles often stay attached to the filaments as a mark of their catalytic origin, as visible as black points in another

TEM study (figure 2) published in Russian at about the same time (Radushkevitch & Lukyanovich, 1952). The paper went unnoticed by Western scientists. In retrospect, many have claimed that the micrograph, which shows a 50-nm wide inner cavity, is the first image of multi-wall nanotubes ever seen (Monthioux & Kuznetsov, 2006).
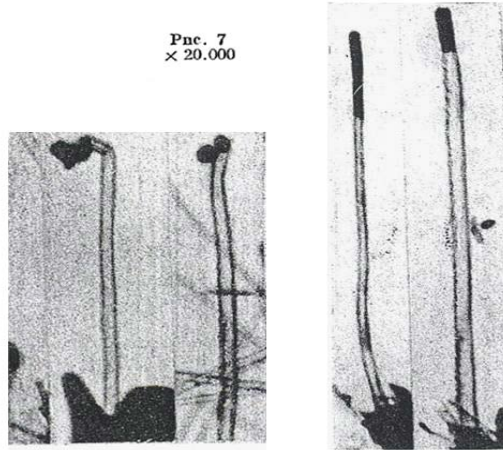
Figure 2 - Micrographs of iron-catalysed carbon filaments (Radushkevitch & Lukyanovich, 1952). (Original Russian Edition Copyright © by Nauka Publishers of the Russian Academy of Sciences. Copyright © 2010 by Pleiades Publishing, Ltd.)

"Filamentary growth of graphite has recently been rediscovered" reads a 1958 crystallography paper (Hillert & Lange, 1958). Focusing an entire instrumental arsenal on the filaments (TEM, polarized light microscopy, X-ray and electron diffraction), the crystallographers make clear that the filaments are hollow, built up of lamellar units bent into cylinders, single or multi-wall, with thicker threads formed by radial growth. They display a variety of shapes while having all the same crystalline structure, graphite. The thicker threads are produced by a two-step mechanism: first, catalyzed growth of an individual filament; second, catalyst-free pyrolytic carbon deposition thickening the fiber.

In retrospect this 1958 paper reads like an anticipated description of carbon nanotubes. Some even claim that carbon nanoscience is only a rediscovery of phenomena that have already been observed but fallen into oblivion (Boehm, 1997; Monthioux & Kuznetsov, 2006; Monić, 2011;

Hoffmann *et al.*, 2016)[3]. By the 1950s, it had been established that a hollow carbon tube could be produced by catalytic growth. But did it constitute a matter of interest?

Actually, these retrospective readings highlight less some obscure forgotten precursors prone to reduce the revolutionary claims of nanotechnologists than the obscuring effects of research programs. Indeed, in the 1950s catalytically-grown carbon filaments could have become a research field in its own right if the thin filaments had not been eclipsed by the bigger carbon fibers.

The "graphite whiskers" obtained by physicist Roger Bacon by vaporizing hydrocarbons in electric arc discharge at high pressure and temperature were roughly the same objects (Bacon and Bowman, 1957). To Bacon, they were "scrolls": concentric tubes made of a rolled-up graphite (figure 3). It has been suggested decades later that they were been multi-wall nanotubes, not "scrolls". Bacon lucidly recognized "I may have made nanotubes, but I didn't discover them"[4].
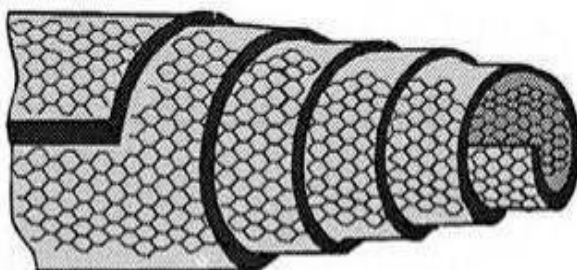
Figure 3 - Bacon's scroll model of graphite whiskers. (Source: http://what-when-how.com/nanoscience-and-nanotechnology/carbon-nanotubes-and-other-carbonma terials-part-1-nanotechnology/)

One can observe without discovering. The famous Archimedean *eureka* does not proceed from mere visual evidence obtained through powerful instruments but from a context-dependent disposition of mind. Unlike chemists who examined the formation of the turbulent filaments in blast furnaces in order to get rid of them, Bacon was working for a chemical

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[3] To remedy this situation a database of carbon allotropes with original bibliographic sources is now being established: http://sacada.sctms.ru/

[4] https://www.eurekalert.org/staticrel.php?view=acslandmark090803

company producing high-volume polymer commodities, Union Carbide. These filaments, which could bend and kink while remaining unbroken, could serve to make bigger and even more robust materials.

Yet reinforcing fibers became strategic during the Cold War period when major space and military programs required the manufacture of materials combining the lightness of plastics with the hardness of steel and the strength of ceramics. Bacon's whiskers served right away as precursors of the "carbon fibers" industrially mass-developed since 1963 as a reinforcing structure for composite materials. Dubbed "the new steel", carbon fibers won the competition among materials hands-down: with their high elastic modulus and low density and rigidity, when inserted in epoxy or polyamide resins they offered performance five or six times higher than aluminum or titanium alloys. Supersonic planes, helicopter tails and blades, rockets, Formula One cars, sports equipment… carbon fibers were strategic, high-performance and capitalistic – relatively expensive – materials for a proud industry employing armadas of materials scientists and engineers (Bensaude Vincent, 1998, p. 178-180).

The success of carbon fibers increased the clandestine status of their precursors, the carbon filaments. Hitherto encountered as anomalous by-products of steel production, they were now eclipsed by "the new steel". When found once again on carbon arc anodes (Wiles & Abrahamson, 1978), they were identified as "carbon fibers from about 4 nm to about 100 nm". They were not different objects, but smaller objects of the same kind. Of course, they kept on popping up, but in rather old-fashioned fields such as Soviet "metallic science" (Nesterenko *et al.*, 1982) or marginal research such as heterogeneous atmospheric chemistry (Buseck & Bradley, 1982). Again, they were quickly forgotten.

An Academic Material: Graphene

By the mid-20th century graphite was a highly strategic material for the nuclear industry, with no less than 11 uranium-graphite-gas reactors built in France in the 1950-60s. While nuclear graphite occupied the forefront of the technomilitary scene (Walker, 1962), a more discrete but no less strategic existence opened up to graphite in the fabrication of intercalation compounds (Teissier, 2014, p. 253-254).

Graphite is made of stacked layers held together by weak van der Waals forces, each layer constituted of hexagonally-arranged carbon atoms linked by strong covalent bonds. Because of its lamellar structure, graphite is able to take up atoms, ions, molecules, or even metallic alloys by expanding the space between the planes while maintaining its structure unchanged.

Due to its chemical properties (both oxidizing and reducing) graphite exchanges electrons with its intercalated guest. These intercalation compounds are used in the manufacture of electrodes and batteries, such as the lithium-graphite compounds forming the negative electrode of lithium-ion batteries in our mobile phones and laptops.

The individual layer of graphite was isolated in the early days of intercalation compound research by German chemists Hans-Peter Boehm and his colleagues (Boehm *et al.*, 1962). While the preparation of these "thinnest carbon films" required astute chemistry, the resulting "lamellar carbon" was not a matter of interest for itself but rather a "test object" (Mody & Lynch, 2010) used for calibrating TEM lattice imaging[5] or possibly an interesting catalyst (Boehm *et al.*, 1963).

Boehm forged the term "graphene" (from *grap*hite + benz*ene*) in the 1980s for denoting a single layer of hexagonal carbon (Boehm *et al.*, 1986). His definition was formally adopted in a 1994 IUPAC nomenclature for graphite intercalated compounds and officially endorsed in the 1997 *Compendium of Chemical Terminology* (McNaught & Wilkinson, 1997).

Carbon filaments had no proper chemical name but were designated by a compound term ("graphite filaments", "fibrils", "vermicules", or "whiskers"). On the contrary the IUPAC *Compendium* stressed that "it is not correct to use for a single layer a term which includes the term graphite, which would imply a three-dimensional structure", and consequently that "the term graphene should be used only when the reactions, structural relations or other properties of *individual layers* are discussed". Thanks to Boehm, the *two-dimensional plane* composing three-dimensional graphite had a name and a material identity of its own. "Graphene" became a common term to refer to the single sheet of graphite in the well-established and industrially-relevant field of carbon intercalation. Naming matters.

Moreover, the name denoted something that many solid-state chemists and physicists were familiar with: the perfect chicken-wire monolayer structure they were trained to *draw* for decades. Thus, before earning a name of its own graphene pre-existed as a theoretical paper model for understanding the chemistry and physics of graphite. It was used to calculate the band structure of graphite from the 1940s onwards and provided a paradigmatic case study to teach band theory (Pisanty, 1991). It was a "paper material", a structural component virtually involved in higher-dimensional graphite and an abstract model used for many scientific purposes, but materialized only in paper drawings.

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[5] See http://zfn.mpdl.mpg.de/data/Reihe_B/17/ZNB-1962-17b-0150.pdf (p. 2).

This did not prevent researchers from getting graphene crystals at the bench, either as "overlayers" grown by epitaxy on a metallic substrate, "pancakes on a plate" etched or sliced into individual layers, or in the form of rolls, cones, or folded like an origami, which minimizes their surface energy – each time in a particular disposition or supported by a surface, never in its free state. Thus academic graphene lived a kind of dual or Platonic existence as an intelligible form and an imperfect copy.

A Speculative Molecule: The Carbon Balloon

If graphene was an academic material, the nanomaterial known today as "fullerene" (C_{60}) was first a speculative molecule. Structurally, C_{60} is a truncated icosahedron, a semi-regular polyhedron belonging to the class of the Archimedean solids, which grants it interesting mathematical properties and makes it resonate with an entire esoteric tradition devoted to mathematical cosmography. The figure appears in particular in the illustrations realized by Leonardo de Vinci in 1509 for the *De Divina Proportione* of Luca Pacioli and in Kepler's treatise *Harmonices Mundi*.

The possibility of creating a giant hollow spherical carbon molecule was suggested in 1966 by a fictional inventor known as Daedalus (David Jones). Looking for a solution to bridge the gap between the density of solids and that of gases, he conceived of a hollow molecule that "would be a spherical shell of a sheet-polymer like graphite, whose basic molecule is a flat sheet of carbon atoms bonded hexagonally rather like chicken-wire" (Jones, 1966, p. 245). To do so he proposed to modify the high-temperature synthesis of graphite by doping carbon with defects which would introduce a curvature of the hexagonal plane and close the net into a spherical shell. But Daedalus did not tell exactly which defects would actually do the job. Coming back later to the spherical-molecule problem, he drew on a theorem known as the Euler-Poincaré characteristic[6] and on D'Arcy Thompson (1917), who applied the former to the structure of a microscopic sea creature depicted by Ernst Haeckel, *Aulonia Hexagona* (Jones, 1982). All this erudition served Daedalus to make a single statement: A *pentagon* would serve nicely as the required defect to transform a flat layer

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[6] Euler-Poincaré characteristic is an invariant describing the structure of a topological space regardless of the way it is bent. Denoted X, it is defined as the number of vertices (V) less the number of edges (E) plus the number of faces (F). For spherical polyhedra X is always equal to 2 ($X = V - E + F = 2$). It thus provides a simple rule to transform a sphere into a polyhedron of however many faces one wishes. The truncated icosahedron verifies such a characteristic: $60 - 90 + 32 = 2$.

of otherwise hexagonal lattice into a graphite balloon (figure 4), just like a soccer ball is made of 20 hexagons and 12 pentagons.
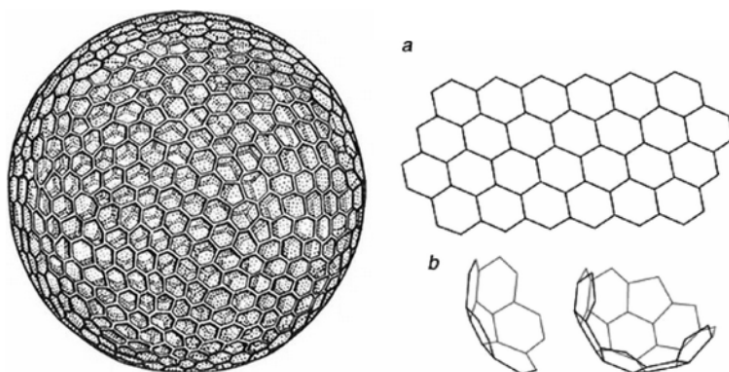

Figure 4 - Haeckel's creature and Daedalus' prediction (Haeckel, 1887, plate 111, fig. 1). (Source: Wikimedia Commons)

In addition to Daedalus' speculations, C_{60} and bigger polyhedral carbon clusters were repeatedly postulated and subjected to theoretical calculations. Japanese computational chemist Eiji Osawa predicted that carbon's structure would then be "superaromatic" (i.e., a conjugated aromatic structure that goes on and on and wraps back to itself) and thus probably stable (Osawa, 1970). He displayed a football image in the publication's front page. Soviet researchers D. A. Bochvar and E. G. Gal'pern (1972) presented the first Hückel calculation on C_{60} and came independently to the same conclusions as Osawa. Several other calculations followed (Davidson, 1981), including a paper entitled "Footballene: a theoretical prediction for the stable, truncated icosahedral molecule C_{60}" (Haymet, 1985). None of these theoreticians cited one another.

Thus, kicked off by the erudite speculations of a fictitious inventor, there was a strange football world cup involving mutually ignorant players. But the carbon balloon, theoretically possible and stable, also represented a synthetic challenge that many chemists believed would soon be at hand. As Cyrus Mody (2008, p. 166) reports, Orville Chapman set several generations of UCLA graduate students to "futile attempts to synthesize 'socchorene' [*sic*] (I_h-C_{60})".

Footbalene, soccerbalene, carbon balloon, soccerane, socchorene… Could we not find a more appropriate name for a molecule on the thre-

shold of existence? In a brainstorming exercise in nomenclature, chemists Josep Castells and Felix Serratosa (1983) attempted to forge a tentative IUPAC name for the hydrogenated species $C_{60}H_{60}$: Hentriacontacyclo[29. 29. 0. $0^{2,14}$. $0^{3,12}$. $0^{4,59}$. $0^{5,10}$. $0^{6,58}$. $0^{7,55}$. $0^{8,53}$. $0^{9,21}$. $0^{11,20}$. $0^{13,18}$. $0^{15,30}$. $0^{16,28}$. $0^{17,25}$. $0^{19,24}$. $0^{22,52}$. $0^{23,50}$. $0^{26,49}$. $0^{27,47}$. $0^{29,45}$. $0^{32,44}$. $0^{33,60}$. $0^{34,57}$. $0^{35,43}$. $0^{36,56}$. $0^{37,41}$. $0^{38,54}$. $0^{39,51}$. $0^{40,48}$. $0^{42,46}$]hexacontane!

But the quest for the synthesis of the carbon balloon never gave any result, until others simply fell upon it.

Fullerene: The Third Allotrope Fallen from the Sky

As an astrochemist, Kroto got interested in the mysterious new diffuse interstellar bands ("the DIBs") detected in the 1970s by radiospectroscopy in the dark clouds of interstellar space. The molecular carrier of the DIBs was – and is still – an astrochemical enigma. From the DIB's spectra it was hypothesized that they might be long acetylic carbon-chained molecules ($[-C\equiv C-]_n$) known for their controversial ability to form "carbine", a hypothetical linear "third carbon allotrope" also known as chaoite or "white carbon" (Kasatochkin, 1967). The existence of carbyne as a solid was dubious because the longer these molecules are, the more unstable and even explosive they become. Kroto thought it was pure "carbon's myth" (Kroto, 2010).

However, in a 1977 study using the Algonquin (Ontario) radio telescope in which he participated, the team managed to successfully detect the vibration frequency of polyynylcyanides HC_5N (H$-$C$\equiv$C$-$C$\equiv$C$-$C$\equiv$N), HC_7N (H$-$C$\equiv$C$-$C$\equiv$C$-$C$\equiv$C$-$C$\equiv$N), and HC_9N, "the largest molecule yet detected in interstellar space" (Kroto *et al.*, 1978). Kroto conjectured that their synthesis might originate from red giant carbon stars. To test this hypothesis he travelled in 1985 to Texas to work with Richard Smalley at Rice University. Smalley and his team had just built an apparatus that, Kroto thought, could nicely simulate the extreme plasma chemistry of carbon stars.

The machine, dedicated to the production and study of metallic and semiconductor clusters (crystals of the size of a few atoms), had no proper name. It was referred to as the AP2, "the second-generation apparatus, a supersonic nozzle in which a high-energy laser strikes a rotating disc of graphite. A chaotic plasma forms at the graphite surface, provoking the vaporization of carbon atoms into a dense and high-speed helium flow. The carbon time-of-flight mass spectroscopy detection of the helium gas emitted by the machine showed very neat spikes indicating the presence of "something" very stable made of 60 carbon atoms and other residual car-

bon clusters. In 1984, another group at Exxon got the same spikes in a larger spectrum with a similar apparatus, built at Rice (Rohlfing *et al.*, 1984). They were trying to understand the undesirable accumulation of carbon on catalysts. But they did not focus on these specific spikes.

Kroto *et al.* (1985) disclosed the newcomer in *Nature*. Instead of proposing a structural formula or a molecular model like any chemistry paper, they were content with a photograph of a soccer ball on Texas grass and named the molecule "buckminsterfullerene" by analogy with the geodesic domes designed by the architect Buckminster Fuller. How could a metaphor ventured on the basis of a unique experiment convince *Nature's* editors and demanding referees? "It was such a beautiful and perfect structure, how could it have been wrong?" Kroto said later (Seeman & Cantrill, 2016).

Above all, the molecule imposed itself by its beauty. The scientific question – whether fullerene's characteristics match the DIBs spectra – faded to the background. Still unsolved today, most fullerene researchers do not care about it – it just gives a nice aura of mystery to stage the molecules floating like celestial spheres in far out space. Although Kroto (1992) kept working on the problem, the mundane object itself – fullerene – has far overcome the scientific question that initially prompted its discovery[7]. Its popular name, associated with the notoriety of Fuller as a visionary architect, has also done much for it (Applewhite, 1995). What if the molecule had borne the impossibly awkward IUPAC name?

Right after the release of their *Nature* report, the group was told that the structure had already been postulated and calculated several times, although they were the first to have *claimed* (since there was no experimental confirmation of the structure) its synthesis. The discovery of Daedalus' speculations attracted Kroto's attention to the consequences of the Euler-Poincaré characteristic for fullerenes, namely that all fullerenes of any size have 12 pentagons – a magic number for all the family of fullerenes!

Fullerenes, however, were not so much hyped at the moment. They remained "a puff in a helium wind" (Harris, 1999), not a material but a trace detected in a gas obtained in a unique home-made instrument whose result could barely be replicated. Fullerenes could well have experienced a fate similar to the series of other putative "third carbon forms" like carbyne or hexagonal diamond (Bundy & Kaspers, 1967; Hoffmann *et al.*, 2016) – namely, oblivion. But they really took shape and became a hot topic five years later when Wolfgang Krästschmer managed to produce *solid* C_{60}

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[7] At least for Kroto, since Smalley (1997) had other motivations and tels another story, related to semiconductor and metallic clusters for microelectronics (see Cyrus Mody's chapter in this volume).

(Krätschmer *et al.*, 1990). Now the new form of carbon was materialized as a very pure (90% C_{60} and 10% C_{70}) and beautiful plate-like crystal called "fullerite". Since it was able to form a solid, a new carbon allotrope was added to graphite and diamond: fullerene, "the third man" (Kroto, 1993). Of course this "new" carbon was probably here long ago, widely distributed in the universe from stars to soot. But it did not exist as a technoscientific object until a method was established for producing macroscopic amounts of it with a simple technique accessible to any laboratory: a graphite electric arc.

From then on, it multiplied and contributed to engendering a new world of low dimensions: the world of nanocarbons. Fullerene, being zero-dimensional, can be considered its starting point. The genesis of nanotubes – 1D – will now be examined, before turning to graphene – 2D. All these materials existed before: the turbulent carbon filaments, the academic graphene, the speculative carbon balloon. But by the 1990s their mode of existence shifted to technoscientific objects. As they came to interweave their life stories and mutually refer to each other, these objects have helped to unfurl a space of indefinite technological possibilities saturated by promises of radical novelty also known as the "nanoworld".

Nanotubes: From Brand to Bench

Hidden in the bulk of the carbon fibers, the filaments came out of them transformed. But only with the help of fullerenes could they stabilize their new mode of existence.

First manufactured from coal or petroleum pitches, high-quality fibers were then industrially produced mainly in Japan from PAN (polyacrylonitrile $[C_3H_3N]_n$), known as "acrylic" when used in synthetic clothes. The manufacturing process, which requires thermosetting, carbonization, and then graphitization, is quite complex and expensive. In the 1970s, Morinobu Endo was trying to find a cheaper alternative to the PAN process by starting from raw materials (benzene). In order to test his new process of "vapor-grown carbon fibers by catalytic decomposition of benzene", he traveled to Orléans in 1974 to work with the French carbon materials scientist Agnès Oberlin and her TEM. The instrument required using very thin fibers by stopping their growth process at an early stage. Endo and Oberlin did so, and of course they rediscovered the filaments with their small opaque catalytic iron particles at the end of their tips.[8] They named this struc-

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[8] Additional testimonies and archive materials can be found in the website "Sciences : Histoire orale": https://www.sho.espci.fr/

ture "hollow tube" or "hollow core" (Endo *et al.*, 1976). For Endo the hollow core was not an anomalous derivative of "real" carbon fibers but the very initial step of their formation process, the "central tube" before the thickening of the fiber. Instead of treating the hollow core as a defect, he viewed it as a crucial structural feature for the mechanical properties of the fiber, its strongest part which "never breaks when the fiber breaks" (Endo, 2002). Hollowness matters.

Simultaneously, the attention of researchers was shifted from the set of *causes* leading to the formation of the filament (the catalytic decomposition of hydrocarbon) to *the effect itself*. For instance, Baker *et al.* (1975) identified "a new mode of filament growth (…) in which the complete detachment of a catalyst particle from the surface of the metal was not a necessary prerequisite". They established two modes of filament growth: "tip growth" (known since the 1950s) and "root growth" (newly characterized). The catalyst activated the filament's growth but in the case of "root growth" it possessed its own dynamics. In other words, the catalyst acted as an *occasional cause* of the filament's growth, a trigger. Then the growing filament starts a life of its own with different possible arrangements occurring during the rolling of graphene: circular, spiral, or helical arrangements controlled by chirality (Nesterenko *et al.* 1982). As a result, the tubular carbon structures came to be considered for themselves, partly independently from their generating causes. Effects overtake defects. Effects matter.

If catalytic triggering and thermal growth are two different processes, then it would also become possible to *decouple* them in order to better control the filament's growth and produce well separated aligned tubules. This feat is claimed in the widely cited US patent claiming "cylindrical discrete carbon fibrils", filed in 1984 and issued in 1987 to Howard Tennent of Hyperion Catalysis (Tennent, 1984). The patent covers a very large area, including multiple kinds of fibrils, compounds, and processes. In addition to applications in reinforcement of composites by embedding of the fibrils in a polymer matrix (a common, mainstream application of carbon fibers), other embodiments were claimed in which the fibrils could enhance the electrical or thermal conductivity of a material, increase the surface area of an electrode or a capacitor, provide a support for a catalyst, or shield an object from electromagnetic radiation. With such a large spectrum of applications (more or less reminiscent of the uses of nanotubes today), it is a root patent, referenced by more than 300 subsequent patents up to today – including by one of the many patents filed by Endo (2002) since his seminal 1986 vapor-grown carbon fiber patent (Endo, 1986). Since the mid 1990s, it has been referenced by many nano-related patents: "nanowhiskers", "nanofiber", "nanofibrils", "nano-composites", and then, by the turn of 2000,

mostly "nanotubes". In contrast with carbon fibers, the main industrial tar-get is no longer structural applications but electrical ones: conductive mate-rials for microelectrodes, batteries, coatings and inks, and electrochemical cells.

When Sumio Iijima (1991) published the observations that led him to be credited for the "discovery" of nanotubes, their industrial uses were already widespread.[9] Nanotubes thus already had a rich "brand existence" at the factory, developed well before and rather independently of the emer-gence of an academic community gathered around them. So Iijima defini-tively did *not* discover carbon nanotubes in 1991, but he brought them *back* to the attention of a wider audience on the academic scene.

Fullerenes played a crucial role in the academic rebirth of nanotubes. Iijima had closely followed the irruption of the "third man", Mr Buckmins-terfullerene (Iijima, 1987). His 1991 paper starts with the invocation of ful-lerenes and reports having used the same graphite arc-discharge method as Krätschmer *et al.* (1990). The only thing Iijima did differently was to look not into the sooty deposit collected in the evaporation vessel but onto *the graphite electrodes* used to generate the arc-discharge themselves. As if the pa-per said "Hey, look over here, not there!" Then any researcher that had al-ready tried to make electric-arc fullerenes according to the Krätschmer me-thod could look again at the used graphite cathode discarded as junk to find similar tubes. The simplicity and wide availability of the experimental sys-tem affording nanotubes partly explains why so many researchers pay a huge tribute to Iijima's 1991 report. Its popularity cannot be attributed to the magic power of the prefix "nano" since there was no "nano" in it.[10] It reads "helical microtubules", "needle-like tubes", or "graphene tubules". The paper does not promise a bright future for industrial applications; ra-ther, it simply describes tubes obtained by electric arc. This point is crucial: the thing of interest was to be found on the *generative part* of the experimen-tal system – itself made of carbon (graphite electrodes) – not in the evapo-ration vessel where the *products* of electric arc discharge are usually collected. The thing coincides with its genesis.

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[9] Endo (2002) for instance was already mass-producing multi-wall nanotubes for electric batteries for more than a decade when he learnt – much to his stupefaction – that they had been "discovered" by his Japanese colleague.

[10] The term "nanotube" was coined as short form for "hollow graphitic tubules of nanometre dimensions" by the Franco-Norwegian physical chemist Thomas Ebbe-sen, working at the same time as Iijima in the same research institution (Tsukuba Fundamental Research Laboratories of NEC Corporation) in a 1992 paper report-ing "large-scale" synthesis (gram quantities) of these objects (Ebbesen and Ajayan, 1992). Iijima only began using it in 1993 (Iijima and Ishahashi, 1993).

Of course Iijima did not discover carbon nanotube first, but in a way "he discovered them *best*" (Jones, 2011). His main accomplishment was a twofold operation of deterritorialization and reterriorialization[11] through which the tubes changed their mode of existence. The paper considered the tubes for themselves, regardless of their industrial uses, as unique individual entities growing without catalyst and hydrocarbons – only from graphite. He insisted on the relation between helical pitch, growth process, and electron diffraction patterns which suggested that the tubes might have unique electronic and mechanical properties with regard to their different helical conformations. The paper also broke the ties that bound carbon tubes to carbon fibers more than Endo did. Endo viewed hollowness as a structural feature responsible for the stiffness of a bigger fiber. Iijima valued hollowness as a functionality afforded by the tube, an affordance in the sense of a possibility of action offered to an agent by an environment (Gibson, 1979). Hollowness affords helicity, and helicity in turn affords new mechanical, chemical, and electronic behaviors. He also viewed Bacon's "scroll growth" model (which explained the formation of the carbon filaments at the origin of electric arc-evaporation carbon fibers) as inadequate since no edge overlaps were observed at the needles' surface, and replaced it with a "spiral growth" model aided by the chirality of the formative steps.

The divorce with Bacon's growth model for carbon fibers did not just cut the hierarchical link between the two objects (deterritorialization); it also provided a new reinterpretation of their relationship (reterritorialization). Since Bacon's scroll model is false, then Bacon's "graphite whiskers" should have been multi-wall nanotubes, not scrolls.

Thus, Iijima deterritorialized the tubes from carbon fibers as well as from any field of application, and reterritorialized them onto fullerenes. His tubules were indeed finite structures closed by two hemispheres, and so fullerenes were both materially and symbolically capping the tubes. Thank to them their genesis was completed, looping back on itself. They could exist fully as individual objects in their own right (deterritorialization), while establishing structural and generative relationships with the other nanocarbons with which they appear in forming a family (reterritorialization). Fullerenes contributed to making the tubes more real and more attractive while, in turn, the tubes helped bring fullerenes the Nobel prize in 1996.

The tubes also helped make graphene more prominent. The existence of graphene was already implicated, *enveloped* in that of fullerenes and

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[11] Deterritorialization (Deleuze & Guattari, 1972) describes any process by which a set of hierarchical relations are broken and set free from their context of emergence to allow their actualization in different contexts (reterritorialization).

nanotubes as the virtual plane necessary for their mental reconstruction, the surface required for their design, their generative matrix. This is visible in the diagram displayed in Iijima's 1991 report (figure 5), as well as in two papers co-authored by Mildred and Gene Dresselhaus *et al.* one year later (Dresselhaus *et al.* 1992a, 1992b). The first explains the formation of fulle- renes "by their projection on a honeycomb lattice" (i.e. graphene), and the second accounts for the structure (both topologic and electronic) of "*gra- phene* tubules" based on fullerenes.
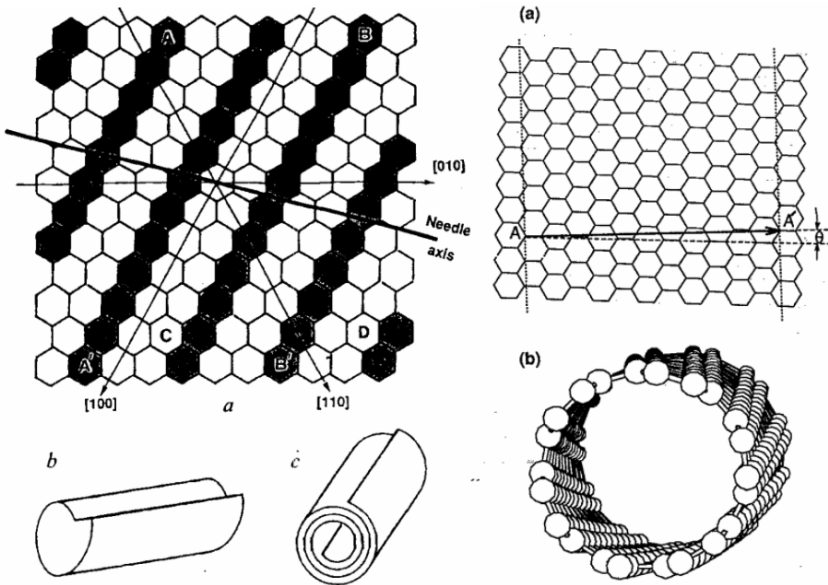

Figure 5 - From plane to tubes. Left: Spiral growth and scroll growth explained from graphene. Reprinted by permission from Macmillan Publishers Ltd: Nature (Iijima, 1991)[12]. Right: How to make a chiral tube from graphene. Reprinted by permission of APS http://dx.doi.org/10.1103/PhysRevB.46.1804 (Dresselhaus et al. 1992b)[13]

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[12] The Iijima's caption of (1991, p. 57) caption reads "*a*, Schematic diagram show- ing a helical arrangement of a graphitic carbon tubule, which is unrolled for the purposes of the explanation. The tube axis is indicated by the heavy line and the hexagons labelled A and B, and A' and B' are superimposed to form the tube (…). *b*, The row of hatched hexagons forms a helix on the tube. (…) *c*, A model of a scroll-type filament".

[13] "The vector *AA'* specifies a chiral fiber. We connect two dotted lines, normal to *AA'* at *A* and *A'* to form a chiral fiber" (Dresselhaus *et al.,* 1992b, p. 46).

It was in these 1992 papers that Dresselhaus transposed the topological "zig-zag/armchair" language from organic chemistry into carbon materials science. For nanotubes, zigzag and armchair are two specific non-chiral topologies located at the endpoints of an indefinite range of chiral topologies having various helical pitches. But this armchair-or-zigzag character also gathers together the three main nanocarbons within a generative topology by which they all shape each other. The way C_{60} fullerenes are cut affords armchair or zigzag tubes, and enucleating the end hemispheres of chiral nanotubes affords fullerenes of different specific geometries (figure 6). Similarly, rolling graphene in a zigzag or armchair way affords different specific tubes.
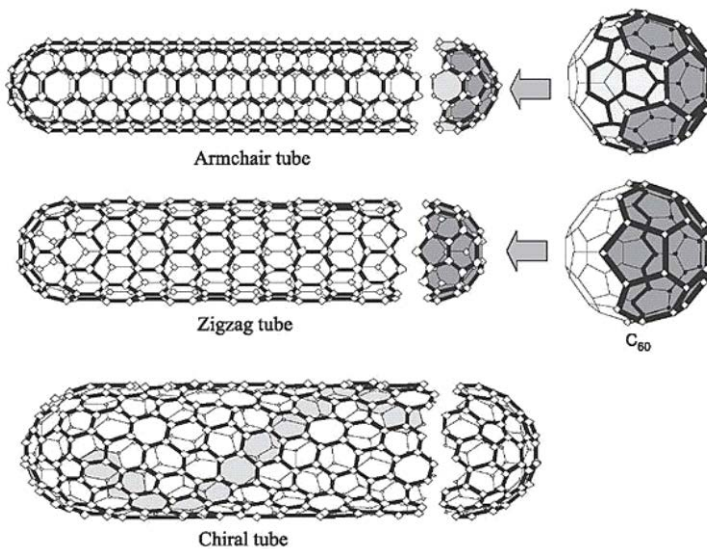
Figure 6 - The structure of armchair and zigzag graphene tubes (adapted from Dresselhaus et al., 1995). (Source: http://what-when-how.com/nanoscience-and-nanotechnology/carbon-nanotubes-and-other-carbon-materials-part-1nanotechnology/)

In the period following the publication of Iijima's observations a growing number of materials physicists and carbon scientists jumped on the electronic properties of nanotubes and embarked on the task of determining their band structure. But how to do so since the number of possible nanotube structures is theoretically infinite? Such was the role played by the nomenclature invented in 1992 by one of Iijma's colleagues at NEC Semi-

conductors labs, physicist Noriaki Hamada (Hamada *et al.* 1992). Hamada's notation (figure 7) was a crucial contribution, used right away in most of the nanotube papers that would follow.
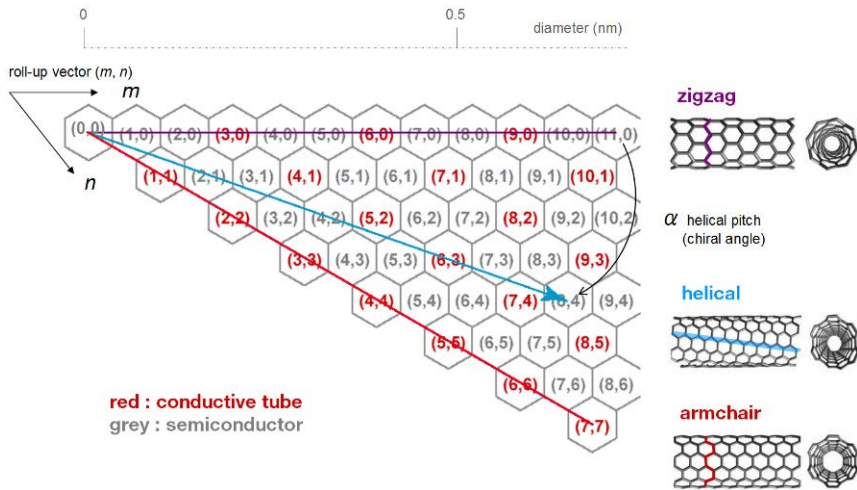

Figure 7 - Hamada's notation
(Source: picture processed by the author)

A combination of two numbers, *m n*, defines a vector on graphene lattice. This "roll-up vector" uniquely identifies all specific types of nanotubes. Zigzag nanotubes are those in which one of the two indices = 0, armchair nanotubes those where *m = n*, all other types are chiral. This vector determines the orientation of the tube circumference and its "helical pitch" α. Thus, each type of nanotube of any circumference, length, and wrapping angle can be specified by a simple index of only two numbers.

But Hamada did more than establish a convenient nomenclature: he showed how theoretical predictions of electronic properties match this index. All armchair tubes are expected to be metallic; zigzag and helical tubes are semi-conductors except if *m* minus *n* is a multiple of 3 (then they would be metallic).[14] Thus, the electronic properties would depend sensitively on the wrapping angle. Moreover, it was also predicted that the band gap would depend on the tube's diameter, so that the electronic behavior could

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[14] Dresselhaus (1992b) came independently to the same predictions with a less convenient nomenclature.

be tuned by pushing or bending the tube, which was later confirmed by experiments (Wilder *et al.*, 1998).

To understand the meaning and scope of this notation, it is instructive to compare it with the nomenclature established decades ago for intercalated graphite staging phenomenon, i.e. the fact that intercalated layers are periodically arranged in a matrix of graphite layers (Dresselhaus & Dresselhaus, 1981, p. 4). Like Hamada's notation, the symbolic index corresponds to a schematic diagram that can be drawn on paper.[15] Both languages are symbolic indexes linked with a structural representation of trivalent carbon structures. However, they are very different in that Hamada's notation is not a rigid language of *characterization* but a *design language*. In the former, substituting a β layer to an α layer, for instance, is forbidden. The rigid rules of the stacking phenomenon would not allow for it. By contrast Hamada's language indicates how to roll a graphene sheet with a *chosen* lattice point superposed on the origin to form any nanotube having the desired geometry and electronic properties. It is both a nomenclature and a tuneable *recipe*, an invitation to make a virtually infinite number of possible tubes with predictable electronic behavior.

Allowing the specifation of an infinite number of nano-objects having well defined properties, Hamada's notation opened a field of possibilities that is beyond imagination. This partly explains the blossoming of promises about a new revolution in nanoelectronics that arose during the 1990s.

Graphene: Extreme Carbon Reborn

We have seen that graphene was not discovered in Manchester University by Geim and Novoselov. The Nobel Prize in Physics awarded in

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[15] The notation allows classifying graphite intercalation compounds by a "stage index" n denoting the number of stages graphite makes before finding an intercalated layer. Latin letters ABC refer to the three possible "profiles" of graphite layers,

      A: OO–OO–O
      B: O–OO–OO
      C: –OO–OO–

Greek letters α, β, γ, δ are the "stacking indices": the four possible configurations of the guest species contained in the intercalated layers. For instance, a stage $n=1$ graphite intercalation compound is arranged in a periodical stacking sequence AαAβAγAδ, a stage 2 compound is arranged in a ACαCBβBAγ sequence and a stage 3 compound in a AαACAβABAγ. There are thus definite relationships between the staging index and the stacking sequence.

2010 honors their "ground-breaking experiments regarding the two-dimensional material graphene". What were the experiments that marked its entrance into a new existence, the rebirth of graphene?

The "Random walk to graphene" is nicely recounted in Geim's Nobel lecture: two Russian physicists, tired about the monotony of solid-state physics and looking for fancier science in "Madchester"; an inexperienced Chinese PhD student; a Ukrainian scanning tunneling microscopist; and British scotch tape (Geim, 2010). Three initially unarticulated "thought clouds": Geim's own youthful dream of "metallic electronics", his daze from all the fuss about carbon nanotubes, his reading of a thorough review of Dresselhaus on graphite intercalation compounds (1981), and his observation that despite the maturity of the field little was known about thin films of graphite. So Geim proposed a not-too-hard project for his PhD student: try to make graphite as thin as possible and see what would come from this idea. The suggestion to use scotch tape came from Oleg Shklyarevskii, an STM colleague from Ukraine working nearby on a fellowship. STM researchers customarily used highly-oriented pyrolytic graphite (HOPG) to prepare a standard reference test for STM imaging. In doing so, they would prepare a fresh surface of HPOG by removing a top layer with sticky tape, but they never paid attention to the stuff thrown away with the tape!

However, they did not get the Nobel Price only for this "MacGyver exploit". Whereas all previous incarnations of graphene were observational, they moved straightaway beyond observation and crafted a device showcasing the extreme tunability of its electric resistivity from a conducting to an almost semiconducting behavior. It was the end of the dual mode of existence of graphene: pure theory, impure incarnations. The two merged into a single new mode of existence. The "academic material" was turned into a technical device.

The Manchester team also claimed to have isolated *freestanding* graphene (Novoselov *et al.* 2005), although Peierls and Landau stated that 2D crystals cannot exist in their free state. According to them, instead of getting graphene in a particular and context-dependent incarnation, they showed and valued graphene "for what it really is":

> After all, we now know that isolated monolayers can be found in every pencil trace, if one searches carefully enough in an optical microscope. Graphene has literally been before our eyes and under our noses for many centuries but was never recognised for what it really is. (Geim, 2010, p. 88)

But what is it that graphene "really is"? First and foremost, graphene is a pure surface. Prior incarnations never involved freestanding graphene

as a self-sustained surface. Now the surface was deterritorialized, freed from the volume, freed even from the "*of*" (it is no more the surface *of* something… other than itself): a "surface in-itself" and no more an "over-layer" on the top *of* something or standing *on* something. As a scientific blogger nicknamed "Carboffiliac" put it:

> It is clear that the graphene films that Boehm et al made are not freestanding graphene, since they are in a dilute alkaline solution – hence at best they are free-floating, not freestanding, and if you don't know the difference, try standing on water, only few have accomplished that! (Carboffiliac, 2009)

What does "freestanding" mean for those who, like Geim, Novoselov, and many Carboffiliacs, sing this "ode to one" (Geim, 2010, p. 90)? Strictly speaking, it is not about standing in empty space like the Holy Ghost. In Carbofilliac's joke, Jesus, unlike the Holy Ghost, can stand *on* something (walking on water) while still being "freestanding" (maintaining His walking behavior instead of swimming). Similarly, "freestanding graphene" refers to the ability of graphene to be reterritorialized in various contexts, transferred from one kind of substrate or environment to another while still maintaining its distinctive high "quality".

Indeed graphene beats records in electron mobility, with conducting electrons behaving as massless particles much like photons, even in ambient conditions. For optics it absorbs light over a wide spectrum from infrared to ultraviolet. It is both nano and macro and can be engineered at both scales. It can potentially make membranes, flexible screens, conductive ink, transparent electrodes, magnetic shielding… In short, graphene fully meets the objectives of nanotechnologies as it is *par excellence* an "enabling material". But even more is expected from it: a technological breakthrough not yet thinkable, for what distinguishes graphene from all known materials is less its performances taken one by one than the unique combination of "qualities" it affords.

Remarkably, graphene scientists often speak about its electronic, mechanical, magnetic, optical, or chemical "qualities" instead of using the more neutral "properties". No doubt the use of this term shows a concern for valuating graphene and often goes with superlatives: astonishing, mystifying, counter-intuitive (Geim, 2010, p. 89). But beyond the hyperbolic effects this term emphasizes that graphene is *qualitatively* different. For instance, the extremely high amplitude of the electric field effect reported in Novoselov *et al.* (2004) – "thousands of times more than the few per cent changes observed previously for any metallic system" – is said to amount to a "qualitative difference" (Geim, 2010, p. 88). Or else, the properties of the individual monolayer are so different from those of the multiple stacked

layers composing graphite – starting with the fact that it is a surface with two sides, pushing to its extreme the "surface matters" motto characteristic of nanotechnology – that the variation is not a matter of more or less, but one of sameness and otherness.

"Quality" is also an old technical term of metaphysics. Unlike *essence* or the *nature* of being (*what* something is), qualities designate the *modes of being*, the *ways* by which something is (*how* something is). Etymologically, qualities (*qualia*) refer to the state of something that is *qua*, "that which is like that". It differs thereby from *essential properties*, that which *define* something. 17th century mechanistic philosophers distinguished between "primary" (solidity, extension, figure, movement…) and "secondary" qualities (colors, odors, heat, textures, but also emotions, feelings and values). Primary qualities are caused by the essential properties of the substance; they are inseparable from its existence but separable from the existence of the perceiving subjects. "Secondary qualities" are deemed merely subjective, inseparable from the existence of their perceiving subject but separable from the substance. What about graphene's qualities?

For a pure surface there is no more ontological difference between the material substance and its surface properties, between primary and secondary qualities, superficiality and depth. There is only a *superficial ontology* – an ontology of surface *qua* surface – wherein the stuff identifies itself with its qualities. Graphene has an intrinsic technical value as a pure surface, a "technicity" in the sense of Gilbert Simondon (1958), which is close to aesthetic beauty. When graphene champions speak of "recognizing graphene for what it really is", they do not refer to an objective substrate that "stands under" (*sub-stare*) the surface and its properties. What graphene "really is" is not its essence but its high "quality", a category that, in this context includes both being and value. The existence of a 2D structure in its free state is both an ontological reality and a technical opportunity, a mode of existence characterizing a "technoscientific object" (Nordmann, 2017). The objective and the subjective, the physical and the social meet on the same plane of existence – on the same surface, one might say.

Conclusion

This chapter suggests that carbon has repeatedly attempted to attract the attention of researchers by deploying a variety of figures: filaments, whiskers, hollow tubes, soccer balls… but their dispositions and affordances remained buried in the black soot of furnaces and their small dimensions drowned in the mass of heavy industry. The nanotubes acceded to existence only in association with fullerenes as heads of a large family of

nano-objects captivating thousands of researchers. In this process, everything happened as if the three main nano-allotropes had mutually been "giving assistance" to each other – which is generally not the case with materials, which are often positioned in fierce competition to conquer markets. Each of them has become more real and more attractive by referring to each other in a space of emotional and material transformations comparable to the system of basic figures that makes the world of painting according to Kandinsky (1929): the point (fullerene), the line (nanotubes) and the plane (graphene).

The analogy conveys several meanings associated with this new mode of existence: that of *artistic quality*, the view of carbon as an artistic material instead of a dumb piece of matter. That also, of a system of *generative geometry*: just as for Kandinsky the line is the result of a living force applied to displace the point in a given direction and the plane is obtained by displacing the line, graphene can wrap into fullerenes or tubes, fullerenes can cap graphene cylinders into tubes, and tubes can be cut into graphene ribbons. *Interobjectivity* matters: just as the figures of painting can be described by their mutual relationships, the analogy allows one to pay – and to attract – attention to the relationships between objects, and not only between subjects and objects (Latour 1991, Harman 2011). Moreover, for Kandinsky, the point is not a mathematical abstraction; it has a certain shape, extension, and affective resonance with regard to its position relative to other objects. The line is a result of a living force with a certain direction and inflexion. As to the surface or "basic plane", to Kandinsky it is not a mere substrate but a living matrix that requires the artist in order to be "fertilized" and to be felt "breathing". Just as Kandinsky's figures take on different affective tonalities shaping the sensibility of the beholder or the artist according to their mutual relationships, the configurations and dimensions of nanocarbons instantiate a *subjective geometry*. This emotional load may explain why fullerenes and nanotubes have (and surely will) remain molecules that matter even if they never deliver the tremendous applications promised over about twenty years of nanoscale research programs (Mody, 2008).

Despite all the proofs of concept for nanoelectronics and the indefinite field of possibilities opened for their design during the 1990s, nanotubes face great difficulty in finding their way to real-world applications while still maintaining their identity as individual nano-objects. Graphene supplants carbon nanotubes in this respect because it offers a homogeneous material, whereas sorting a batch of carbon nanotubes with specified wall numbers and helicity is barely feasible at an industrial scale. However, due to its lack of band gap graphene is not destined to replace silicon. Basic technoscientific research has made considerable progress in recent years

thanks to interdisciplinary mobilization but also because graphene has benefited from all the available nanoscale instrumentation as well as the know-how acquired in the chemical manipulation of carbon nanotubes. But graphene no longer has the right to exist as an academic material; it cannot remain a material on the shelf. Yet the number of cleanrooms, ultra-high vacuum instruments, postdocs, and European funding filling the "Home of Graphene" at Manchester University indicates the amount of means required to maintain graphene "freestanding"! Even if industrial production of large surfaces is possible, graphene cannot be introduced into macroscopic objects without a substrate and then it loses the affordances of the pure surface.

This is to say that the announced revolution may be delayed… However, graphene is also impelling a new movement back from brand to bench. Indeed it is perhaps unique but it is *generic*. Its mode of existence as a pure surface reveals to the possibility in other elements as well. Although it displays a unique combination of qualities graphene is neither perfect nor even optimal for the applications for which it is intended. Depending on the specifications of each sector, research begins to lurch towards other 2-D materials. Performances of the same order can be expected of any material displaying strong bonding within the plane and weak connections between planes. Thus graphene now appears as the head of a new family of 2-D "gigamolecules" including boron nitride, tungsten disulphide, and metal carbides, sulphides or selenides. Two-dimensional ceramic oxides are being made. After deploying a wide range of possibilities and opening the way to a new class of materials, carbon can fade into the background and give way to new competitors.

Acknowledgment

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