Essay Review

Is There Life After Partington?

Pierre Laszlo

S. Reich, C. Thomsen, J. Maultzsch: *Carbon Nanotubes: Basic Concepts and Physical Properties*, Wiley-VCH, Weinheim, 2004, ix + 214 pp., [ISBN 3-527-40386-8].
G. Schmid (ed.): *Nanoparticle: From Theory to Application*, Wiley-VCH, Weinheim, 2004, x + 434 pp. , [ISBN 3-527-30507-6].
C.N.R. Rao, A. Müller, A. Cheetham (eds.): *The Chemistry of Nanomaterials: Synthesis, Properties and Applications*, Wiley-VCH, Weinheim, 2 vols., 2004, xv + 740 pp., [ISBN 3-527-30686-2].
M. Köhler, W. Fritzsche: *Nanotechnology: An Introduction to Nanostructuring Techniques*, Wiley-VCH, Weinheim, 2004, 272 pp., [ISBN 3-527-30750-8].

1. Contents of these books

The book on carbon nanotubes is authored by scientists from the Technical University in Berlin and from Cambridge University. It has eight chapters and an introduction. Chapter 2 deals with structure and symmetry. Single-walled carbon nanotubes have line-group symmetry, *i.e.*, they show translational periodicity only along the tube axis. Chapter 3 is devoted to the electronic properties of single-walled tubes, whose electronic band structure can be calculated rapidly and easily. One third of the tubes are metallic or quasi, the others are semiconductors with moderate band-gaps. Chapter 4 on the optical properties shows isolated nanotubes to be promising candidates for light emitters. Chapter 5 on electronic transport shows so-called armchair single-walled tubes as ballistic conductors in a range of lengths, from 100 nm to 1 μm. Chapter 6 discusses elastic and vibrational properties. Chapter 7, the key chapter, covers the main diagnostic tool, Raman scattering: double resonance dominates the spectrum, much more than in any other solid. And chapter 8 summarizes the take-home lessons: two features, a radial breathing

HYLE – International Journal for Philosophy of Chemistry, Vol. 10 (2004), No. 2, 169-178.

mode and a double-peak structure just below 1600 cm^{-1} characterize nanotubes; the diameter of the tube can be inferred from the frequency of the former; whenever the incident light is polarized along the nanotube axis, the Raman signal is at its strongest; the defect concentration can be measured from the intensity ratio between two peaks; metallic tubes show a broad peak around 1540 cm^{-1}.

The multi (20)-authored book on nanoparticles is, justifiably, centered on the so-called quantum dots. If solid particles become small enough, in the nanometer range, they become electronically comparable to atoms and molecules. Instead of the laws of classical physics, they become quantum systems with discrete energy states. This is the basis for a number of useful applications. Quantum dots are reminiscent of the rhetorical question raised by Greek philosophers in antiquity: consider a sand-heap. If one removes from it a single grain of sand, obviously it is still a sand-heap. One continues doing so. At which stage does the sand-heap become something else?

One of the most exciting applications of quantum dots is the single electron tunneling transistor. An electrometer measures electric charge. A single electron transistor is, at present, the most sensitive electrometer. Small alterations of the charge distribution beneath a small isolated island of aluminum atoms markedly affect the conductivity across that island. When a gate voltage is applied to an electron donor material, such as tellurium, placed underneath the island, changes in conductivity can be monitored.

Nanocrystals are indeed important in single electron devices operating at room temperature, such as supersensitive electrometers and memory storage. Capped nanocrystals of both metals and semiconductors by virtue of their size possess capacitance in the range of attofarads (1 aF = 10^{-18} F). Charging a nanocrystal with an extra electron perturbs it to such an extent that the next electron requires an appreciable change in the charging potential. This is often seen as a 'Coulomb staircase' in the current-voltage tunneling spectra. Indeed, the charging energy varies linearly with the inverse of the diameter of the nanocrystal. Such sensitivity to single electron charging makes a nanocrystal an ideal candidate for use in single electron transistors and memory devices.

There are metallic and there are semiconducting nanoparticles. The former enjoy industrial and medical applications, for their magnetic properties in particular. The latter have uses in electronics and optoelectronics. One can also write with nanoparticles, dip-pen lithography is one of the techniques. More generally, the challenge is to organize nanoparticles in three dimensions.

The natural and the artificial once again meet! Biosystems, such as enzymes, antibodies, and nucleic acids have sizes commensurate with those of man-made nanoparticles. Hence, it becomes tempting to marry and hybridize them into nanocomposites, which is one of the most recent developments.

This is also one of the attractions of the chemistry of nanomaterials book. Another is to remind the reader of a characteristic of the chemical mindset. Two of the main thrusts of nanotechnology have been self-assembled ordered arrays of atoms with specific properties (electrical conductivity, magnetism, *etc*.) and well-defined, molecule-like clusters of atoms endowed with specific properties. The keyword here is specificity.

Little needs be said on the nanotechnology book. It lacks direction and substance.

2. The founding moment

The standard account of the birth of nanotechnologies dates it to the lecture by Richard P. Feynman on December 29, 1959 at the annual meeting of the American Physical Society held at Caltech. The books under review rightfully salute Feynman as the Founding Father of the field. As is well-known, the brilliant Caltech physicist ended his talk with a dare, announcing two prizes financed with his own money for the miniaturization of the pages of a book and for the building of a miniscule electric motor, only 1/64 inch cube.

Feynman's lecture makes interesting reading. [1] Its perspective is identical to that in Jules Verne's books, not visionary in the sense of a prophecy, imagining revolutionary developments and devices. The outlook is much more down to earth. Jules Verne and Richard P. Feynman took heed of recent scientific and technological advances to extrapolate to what the future would almost certainly witness, in a prospective.

In his lecture Feynman took as his starting point the feasibility of scaling down the contents of the world's libraries. He guesstimated their holdings at about 24 million volumes. He figured[2] that their total information could be contained on an area of about 35 pages of the *Encyclopaedia Britannica*. This intellectual exercise of Feynman's had its obvious seed in the then recent (1953) discovery of the DNA double helix by Watson and Crick. If the genome has such a small size, Feynman thought, given the awesome amount of information it encodes, is there anything preventing scientists and engineers from emulating this natural feat?[3]

Let us keep in mind such inheritance. Biology thus gave birth to the whole field of nanotechnologies. To go by the empirical criterion, Feynman's call was that of a pioneer, it went unheeded for a generation.[4]

After Heinrich Rohrer and Gerd Binnig devised in 1981 a scanning tunneling microscope, a collective leap forward ensued. About that time, George

B. Whitesides initiated a series of studies which showed the kind of contributions chemists might make to nanosystems. The nanotechnology bandwagon started rolling in the 1990s. It was pulled by two horses. There was Moore's Law. Engineers and scientists had for decades looked at the horizon of computers foregoing silicon chips in favor of molecular devices. And there was the demographic factor. The steady increase in the number of scientists, which continued well into the 1980s, was unmatched by a corresponding increase in public money. Accordingly, young scientists as a group partitioned themselves between industrial and pharmaceutical work.[5]

3. An offshoot from chemistry or from biology?

That biology gave rise to nanotechnology raises a counterclaim.[6] Whenever a group of chemists discuss nanotechnologies, they remind one another "this is nothing but chemistry, after all". The declaration can be seen as narcissistic, self-centered, and narrow-minded. Nevertheless, it has a degree of truth. Moreover, like any such stereotypic assertion on the part of a group of scientists, it is worthy of in-depth scrutiny.

Let us then assume for the new sub-discipline to be yet another spin-off from chemistry, in like manner to biochemistry, solid-state physics, molecular biology, or materials science. Because of some unfortunate connotations of the word 'chemistry', its ancient roots on the one hand, its age-old associations with explosives, poisons, and pollutants on the other, people have refrained from using it as a label on a field holding both novelty and promise of lucrative applications. Hence, the renaming as nanotechnologies.

Chemists are prompt to recognize in nanotechnologies lines of forces to them familiar and maybe even *passé*. These include colloids and Langmuir-Blodgett films, which have regained a new hold on both scientists' imagination and grantsmanship. At a more fundamental level, though, chemists have injected into nanotechnologies a key notion, that of specificity. Contrary to what is routinely the case in physics, with fractals an example, chemical phenomena fail to obey scale invariance. They are liable to show quite different features depending on the scale of the observation. Indeed, this serves as a dividing line between chemistry as the science and chemistry as the industry. The latter is interested only in bulk matter and in bulk phenomena, whether heat transfer or equations for overall transformations, with more concern for the bottom line in financial reports than for the specific and microscopic (or nanoscopic) mechanisms involved, in catalysis for instance.

However, what makes nanotechnologies a unique and viable hybrid is that their other parent has been, unmistakably, biology. This is an important legacy, all the more so in view of many of the present applications being in areas distant from biology such as electronics, optoelectronics, and other highly applied applications, from cosmetics to self-cleaning windows.

Biological phenomena are a continued inspiration and biological applications are around the corner. The former? While it was known that many organisms orient themselves from the earth's magnetic field, Blakemore's 1975 finding of bacteria from marine marsh muds heading rapidly north was seminal. Blakemore then used transmission electron microscopy to reveal iron-rich crystals, above 100 nm in diameter, in these bacteria. Several crystals would align into chains along their major axis. Frankel, Blakemore, and Wolfe proceeded to report that an unclassified magnetotactic spirillum (MS-1), when cultured in solutions containing ferric salts, precipitated uniform single crystals that consisted of mostly spinel Fe_3O_4. Microbial magnetite and the ferrimagnetic greigite γ-Fe_3S_4, present in magnetotactic bacteria grown in marine, sulfidic environments, are inorganic crystallizations impressive for their quality. The magnetic particles have the optimal single domain size for the specific mineral. Each magnetic particle contains only a single magnetic domain. Moreover, within the magnetosome, the crystals are aligned so that their assembly bears a permanent magnetic dipole, making an effective compass. Biogenic magnetite provides great inspiration to laboratories active in nanotechnology, as for instance the book by Günther Schmid testifies to.

The latter? Innocuous quantum dots (QD) bioconjugates have been injected into *Xenopus* embryos to monitor the development to the tadpole stages. QD label *Xenopus* embryos at different stages and with specific QD intracellular localizations.

4. New wine in old flasks?

But let us return to the attitude of chemists who discard nanotechnologies as a combination of old, well-known chemistry and a public relations ploy to raise money from industry and from granting agencies. Could it be true that the field of nanotechnologies amounts only to renaming a subset of well-established chemical knowledge? Does it lack originality and impetus? Are we dealing with old wine, which time may have started to sour and to make unpalatable and thus needed a new label? Conversely, is this new wine whose novel taste suggests brand-new flasks?

Consider colloidal gold as a test case. Gold nanoparticles have been the subject of considerable attention over the ages. A back-of-the-envelope calculation shows that a small nanocrystal of one nanometer diameter will have as many as 30% of its atoms on the surface while a larger nanocrystal of

10 nm (ca. 1000 atoms) will have about 15% of its atoms on the surface. Metal particles with dimensions in the nanometer scale thus display unusual properties. The mean free path of an electron in a metal at room temperature is in the range 10-100 nm. As a metallic particle shrinks to that dimension, unusual effects might be observed. Indeed, gold nanoparticles of diameters about 100 nm or less appear red, not gold, when suspended in transparent media.

They enjoy an interesting history dating back to the pioneering work of Faraday on the synthesis of gold hydrosols, gold nanoparticles dissolved in water. As one may recall, early in 1856 Michael Faraday (1791-1867) became interested in the interaction of gold with light. Gold leafs show different colors in transmitted light, green, blue, and purple, than they do in reflected light. This observation intrigued Faraday. Together with his friend, Warren de la Rue, he prepared gold films. He started preparation of gold precipitates from reducing with ferrous sulfate a solution of auric salts, made presumably by attack of the metal with *aqua regia*. In so doing, Faraday discovered colloidal gold. This was the subject of intense experimenting and thought. Between the onset of this work, February 2, and its completion at the end of the same year 1856, Faraday wrote in his diary no fewer than 300 manuscript pages (1,160 numbered entries) on this topic. He submitted an article to the Royal Society on November 15, it appeared on February 15, 1857.[7] In general and since Faraday, metal sols possess fascinating colors and have long been used as dyes.

Smaller gold nanoparticles of diameters about 3 nm are no longer 'noble' and unreactive, but can catalyze chemical reactions. Consider nanocatalysts comprised of gold atom clusters, Au_8, Au_4, Au_3Sr, adsorbed at an F center of a MgO (100) plane. The optimal adsorption geometries of the O_2 molecule to these nanocatalysts differ markedly. Another example is from the temperature-programmed reaction spectra of the different products of the polymerization of acetylene on small supported, monodispersed palladium clusters. Striking atom-by-atom size-dependent reactivities and selectivities are observed. Only the three reaction products C_6H_6 (benzene), C_4H_8 (butene), and C_4H_6 (butadiene) form. Remarkably no C_3H_n, C_5H_n, and C_8H_n are detected, indicating the absence of C-C bond scission, as already observed on palladium single crystals and on palladium particles. Up to Pd_3, only benzene formation is catalyzed, reflecting a high selectivity for cyclotrimerization of acetylene. Pd_n clusters ($4 < n < 6$) reveal a second reaction channel by catalyzing in addition the formation of butadiene. The third reaction product, butene, desorbing at a rather low temperature of 200 K, is clearly observed for Pd_8. For this cluster size the abundance of the three reaction products is similar. For even larger clusters ($13 < n < 30$) benzene formation increases with cluster size, whereas the conversion of acetylene to butene reaches a maximum for Pd_{20}. Note that Pd_{30} selectively suppresses the formation of butadiene (see for instance the Nanocatalysis chapter in the book by Rao, Müller, and Cheetham).

What this example of metallic nanoparticles shows, which many of us have always suspected to be true but which conventional wisdom and standard practice – why bother reading any scientific publication older than say five years? – have both condemned summarily, is that casks of old wine connect with containers of the precious liquid from the most recent harvest. New science can be at its most innovative when it grafts itself onto its historical roots. Prediction starts with retrodiction, a point to which I will return.

5. Beyond the hype

Who is most responsible for inflating the nanobubble? Are scientists, journalists, or venture capitalists the guiltiest? Whatever the answer, a host of start-up companies have seen the light of day, and have issued shares. The Yellow Pages will have to make room for quite a few names with the nano-prefix: Nanometrics, Nanogen, Nanologic, Nanopierce, Nanoproprietary, Nanosys, Nanotechnology Development Corporation are just a few.[8] Some universities have invested heavily into setting-up industrial parks specialized in nanotechnology. SUNY Albany and the University of South Carolina are two examples. The promise is there, because some of the devices already made actually work. IBM was able to use a nanotechnique to increase by a factor 20 the amount of memory on a hard drive.

John Wolfe, who started the first nanotech venture-capital firm, compares it to the Internet circa 1993, before Netscape went public. Is it to say that this new bubble is doomed from the start and that it will burst, sooner or later? Assuredly. Is it to say that it will sink without leaving a trace? Assuredly not. Some companies will survive and be lasting. Already, one can differentiate between fly-by-night operations buoyed only by conning the gullible, and reputable firms such as Nanosys doing solid work, and worth investing into. Nanosys collaborates with well-established corporate giants such as Intel, Matsushita, and DuPont. Peugeot-Citroën and Ford inject sub-10 nm CeO_2 nanoparticles into diesel fuel before it is burnt in the engine. This results in an *in situ* catalyst that not only improves fuel efficiency but also greatly reduces the emission of particulates. More than a million automobiles will incorporate that system by 2005 already. The American Federal government is also among the investors in the Nano Rush. Washington is spending \$ 3.7 billion on nanotech research over the next four years.[9]

Conclusions

To this writer, the key issue is representation. Social groups create self-images, they project somewhat different images to the public.

Nanotechnology, as mentioned at the beginning of this essay, arose from one of the icons of the 20^{th} century, the DNA double helix. It was successful, early on, in giving itself a similar and logo-like icon. IBM scientists created it and the advertising arm of the multinational corporation was ready to pounce and was quick to hammer it irreversibly into public consciousness. This is the STM image of a corral of 48 iron atoms placed in a circle of 7.3 nm radius. This particular image has become emblematic of nanotechnologies, at least for the time being. With it, scientists exhibited to the public, not without intense pride, an atom-made fence. What a feat! But this construction can also be seen as an unselfconscious picture of the proverbial ivory tower. In yet another image, nanotechnology proudly depicted in 1990 on the cover of *Nature* its archetype with an STM image of DNA.[10]

Another graphic depiction of nanotechnologies brings up my next point, representation as re-presentation. The cover page in issue number 24 of *Angewandte Chemie International Edition in English,* volume 37 for 1998, was adorned with a schematic representation of the Mo_{132} cluster. Its similarity to Kepler's early model of the universe, featuring the ubiquity of the icosahedron, was emphasized in the illustration.

Thus, nanotechnology in the time of the Millennium rediscovered the microcosm-macrocosm correspondence prevailing in medieval metaphysics. With some modification, needless to say. Humanism is out: a metallic cluster as the nanocosm replaces man as the microcosm. Just as for medieval theologians, the stress is on the unity of nature, on the uniformity of physical law throughout the universe. But physical science has replaced God in Western thought.

One can interpret also the bow to Kepler as one of the numerous reincarnations of the Platonic archetype of the five regular solids, which has marked the history of chemistry in the braudelian *longue durée*: Kepler and the snowflake, the constituent particles of crystalline solids as proposed by René-Just Haüy, molecular shape according to André-Marie Ampère, Achille Le Bel's and Jacobus Henricus van't Hoff's tetrahedral carbon, Alfred Werner's complexes, Aaron Klug's icosahedral viruses and, closer yet to us, Richard Smalley's and Harold Kroto's buckminsterfullerene. Thus, nanochemists gave themselves a self-image of continuity within the geometric, Pythagorean tradition.

Let me sum up with representation as re-presentation. I have been at pains in this review to point to all the aspects of nanotechnology that predated it. Nanoscientists have moved existing pieces to create new patterns.

There is nothing wrong with this efficient heuristics. Discovery is not the only path to knowledge, fame, and riches. But this raises an interesting question in philosophy and historiography, which will be my final point.

Science rewrites its own history, not only as history but as science fodder too. Which should not be construed in the weak sense of Whig history-telling as indulged in by scientists. While it is very much true that scientists, in a Whig perspective, tend to see the past as heralding the present, their purpose is not the mundane one of setting up an artificial history, approximating to a linear genealogy. The nanotechnologies paradigm shows a considerably more interesting attitude. Science reconfigures past events and developments in order to refocus itself into new directions. Such a reshuffling of the past, which of course may be deeply upsetting to professional historians who see their work voided and having to be restarted anew, the undersigned included, is an essential part of the dynamics of science. And it shows historians of chemistry that there is life after Partington.

Notes

1 Feynman, R.P.: 1960, 'There's Plenty of Room at the Bottom', *Engineering and Science*, **23**, 22-36.

2 As befits a physicist he reasoned from orders of magnitude.

3 To quote from Feynman's talk: "The fact – that enormous amounts of information can be carried in an exceedingly small space – is of course well known to the biologists, and resolves the mystery which existed before we understood all this clearly, of how it could be that, in the tiniest cell, all of the information for the organization of a complex creature such as ourselves can be stored. [...] all this information is contained in a very tiny fraction of the cell in the form of long-chain DNA molecules in which approximately 50 atoms are used for one bit of information about the cell." This jibes with my personal recollections: when I arrived in Princeton in 1962, both campuses at the University and at the Institute of Advanced Study were abuzz with very similar talk.

4 For another example of a voice in the wilderness, consider Merrifield's work that gave rise to combinatorial chemistry.

5 Nowadays nanotechnologies are viewed in the exclusive province of engineering, such as mechanical and electrical engineering. This is easily explained by the pressure from lucrative applications downstream.

6 A serious counterclaim. Conjectures abound with other putative parentage. C. Milburn ('Nanotechnology in the Age of Posthuman Engineering: Science Fiction as Science', *Configurations*, **10** [2002], 261-295) puts forward Robert Heinlein's short story "Waldo" which Feynman's friend Albert R. Hibbs, senior scientist at the Jet Propulsion Laboratory in Pasadena, mentioned to Feynman as he was writing down his talk. The conjecture is attractive in principle, scientific concepts so often originate in art and literature. However, Feynman's fertile imagination had no need for an outside seed. This particular conjecture stands on its head Feyn-

man's whole argument. He proposed devices at the nanoscale as both rational and realistic, around the corner so to say. To propose instead that the technoscience, nanotechnology, belongs to the realm of science-fictional fantasy is gratuitous mythology, with a questionable purpose. – True, there is prestigious precedence for the Frankensteinan side of nanoscience. Without going back to Mary Shelley's moral tale, the 1948 Caltech lecture by John von Neumann, on 'The General and Logical Theory of Automata' is noteworthy (in: L. A. Jeffress [ed.], *Cerebral Mechanisms in Behavior*, John Wiley, New York, pp.1-41). In it, the Princeton mathematician conjectured the emergence of unplanned behavior. Above a certain threshold of complexity, the structure of an object might become simpler than the verbal description of its properties. The builder of automata would become unable to predict all of the features of his creature. Hence, the current controversies about the risks associated with nanotechnologies.

7 Faraday, M.: 1857, 'Experimental relations of gold (and other metals) to light', *Philosophical Transactions of the Royal Society London*, **147**, 145-181.

8 "Although many collaborations are in existence today, they are divided too swiftly into areas of the practical and the calculable – and if such areas are not available, the epithets missing, then they are invented: nano, bionano, supranano, nanotec, bionanotec, etc., etc." (Ringsdorf, H.: 2004, 'Hermann Staudinger and the Future of Polymer Research Jubilees – Beloved Occasions for Cultural Piety', *Angewandte Chemie International Edition in English*, **43**, 1064-1076).

9 Surowiecki, J.: 2004, 'Bring on the Nanobubble', *The New Yorker*, March 15, p. 68.

10 Lukens, R.: 2004, 'Historic Nanotechnology', *Chemical Heritage,* **22**, 29.

Pierre Laszlo:
April-October: "Cloud's Rest", Prades, F-12320 Sénergues, France;
October-April: "L'Orée du bois", POB 665, Pinehurst NC 28370, USA;
pierre@pierrelaszlo.net