ELSEVIER

A sightseeing tour in the world of clusters—serendipity and scientific progress

Arne Rosén

Department of Experimental Physics, School of Physics and Engineering Physics, Göteborg University and Chalmers University of Technology, SE-412 96, Göteborg, Sweden

The discovery of the fullerenes in 1985 by Kroto et al. and the development of a method for producing macroscopic amounts in 1990 by Krätschmer et al. opened a new area of carbon research and the possibility of producing new materials with unique properties. The field has developed further with discoveries of nanotubes, metal-filled nanotubes, carbon onions, met cars, and metal-covered fullerenes, all of which have unique properties and possible technical applications. In retrospect, it is in interesting that indications of many unique species have existed before their discovery but have not been recognized. In general, it seems that one is so focused on a given problem that one does not realize how many great discoveries or serendipities are "hidden" in available experimental and theoretical data. In addition to generating a lot of scientific progress, these new discoveries in the field of cluster science, and in particular in carbon species such as fullerenes and nanotubes, have opened up the doors to different areas of science such as mesoscopic physics and modern material science. The general trend is from small to large systems, contrary to the general trend of modern mesoscopic physics or microelectronics where the movement is from large to small. It is especially fascinating how the whole area of fullerene research was initiated to solve problems in astrophysics. Originally, Krätschmer and Huffman intended to explain an observed strong extinction from interstellar dust; in experiments they produced a special carbon soot with a characteristic optical absorption known as "camel hump smoke." Furthermore, the original interest of Kroto was also to solve problems in astrophysics, while Osawa in his original paper on calculations of carbon molecules in organic chemistry focused on how different bonding of carbon atoms would give special species. He then found the truncated icosahedral built up of sixty carbons, without noticing its unique structure, which is today the famous C_{60}.

Keywords: clusters, fullerenes, nanotubes, astrophysics, nano-technology, periodic table

EARLY CLUSTER RESEARCH

Research on clusters during the past twenty years[1–12] has generated a new interdisciplinary field in which knowledge from many disciplines such as nuclear, atomic, molecular, astro and solid-tate physics has been very valuable. It is presently possible to produce free and deposited clusters, ranging from a few atoms to a few thousand of atoms for many elements in the periodic table. In many cases these clusters have been characterized with respect to different electronic properties, and in a few cases the geometrical structure has been determined using experimental methods developed in studies of atoms, small molecules, or solids. The knowledge obtained from such studies, as for example the experimental discovery of the icosahedral packing in clusters of xenon in the group of Recknagel in 1981,[13] initiated a new direction in the earlier established field of small particles. Probably even more exciting was the discovery of magic numbers for clusters of alkali elements by Knight and colleauges in 1984.[14] Their discovery verified an earlier prediction by Ekardt[15] of the existence of electronic shell structure for the delocalized electrons in clusters of alkali elements. The further development of the so-called self-consistent jellium model[11,12,16] for treatment of systems with a large number of fermions have resulted in many exciting discoveries such as magic numbers, super shells,[17,18] and clusters characterized by shells of atoms,[19] where the direction of research is from small to large units, i.e., from atomic/molecular physics to solid-state physics. This kind of exploration is opposite to the trends in modern mesoscopic physics, microelectronics, nano technology or materials science,[20,21] where the general direction today is a movement from large to small.

Corresponding autohor: A. Rosén, School of Physics and Engineering Physics, Department of Experimental Physics, Göteborg University and Chalmers University of Technology, SE-412 96, Göteborg, Sweden. Tel.: 031-772-3295; fax: 031-772-3496.

E-mail address: arne.rosen@fy.chalmers.se

Journal of Molecular Graphics and Modelling 19, 236–243, 2001

655 Avenue of the Americas, New York, NY 10010

1093-3263/01/$–see front matter
PII S1093-3263(00)00117-0

CARBON CLUSTERS—FULLERENES

The discovery in 1985 by Kroto et al.[22] in their studies of carbon clusters, and the observation of a characteristic peak in the mass spectrum of laser vaporization of graphite initiated a new area of cluster research, which has been highly interdisciplinary in nature. They proposed that the observed peak was due to the existence of a new molecule, C_{60}, in the form of a closed cage structure that resembles a soccer ball or truncated icosahedral with sixty vertices, twelve pentagonal faces, twenty hexagonal faces, and ninety carbon–carbon bonds. Such a spherical structure, with all sixty carbon atoms at the same distance from the center, was estimated to have a diameter of 7Å and an empty cage where any atom in the periodic table could fit and be trapped. This new species was expected to have many unique properties, but also similarities with the known forms of carbon, such as graphite and diamond. This new form of carbon should, for example, have the usual electronic and spectroscopic associated features which are known as π and σ character, originating from the 2p electrons of carbon, but should also have very special characteristics due to the spherical symmetry and curved surface.[23] In the recognition of Buckminster Fuller and his construction of geodesic domes, the new C_{60} molecule was given the name "Buckminsterfullerene." The original work of Kroto et al.[22] had no reference to earlier work in the field. A more detailed survey of the literature showed, however, that in 1970 and 1971[24,25] Osawa had published papers in Japanese with the corresponding title in English, *Superaromaticity*, in which he presents a figure with a truncated icosahedral corresponding to C_{60}. Unfortunately, Osawa himself did not realize the unique features of this species. Furthermore, the scientific community did not recognize this work, since it was only published in Japanese.

Before 1985, Rohlfing et al. at Exxon[26] and Bloomfield et al. at Bell Labs[27] had also used the laser vaporization technique of Smalley[28] and studied clusters of carbon containing up to hundreds of atoms. Even though C_{60} and C_{70} appeared to be somewhat more abundant in the mass spectrum, the significance of this observation was not recognized at that time.

The quantities produced with the laser vaporization technique[28] were, however, not sufficient to verify the proposed structure of C_{60} and it was evident that a new development was necessary. This was discussed by Kroto et al.[22] in their original paper. A number of techniques were probably tried by different groups to produce macroscopic amounts of C_{60}, but without success. Three years before the discovery of C_{60} in 1985, Krätschmer from Heidelberg and Huffman from Arizona started[29,30] to produce carbon particles using a standard technique with an electric arc in He atmosphere, normally used for production of nm-size carbon particles. The grain material that they produced was characterized using different spectroscopic techniques such as Raman, IR, and UV-visible spectroscopy.[29–31] At a certain He-quenching gas pressure, strong peaks appeared in the UV-visible as well as in the infrared. Krätschmer and Huffman named the additional features, above the broad background, in UV and visible "camel hump smoke" without knowing the origin of these peaks. They started the experiments due to their interest in astrophysics, in particular to explain a very strong extinction in the UV region of interstellar dust[32] as reproduced in Figure 1. The dominating feature is the broad peak centered around 217 nm or 5.7 eV. This famous extinction was observed during the late 1960s[33] and its original explanation, based on calculations,[34] was that it was due to small spherical particles with optical properties similar to those of graphite.[35] Early experiments[36] using the same evaporation technique also showed similarities to the interstellar extinction, but since the fit was not perfect the problem was left unresolved.

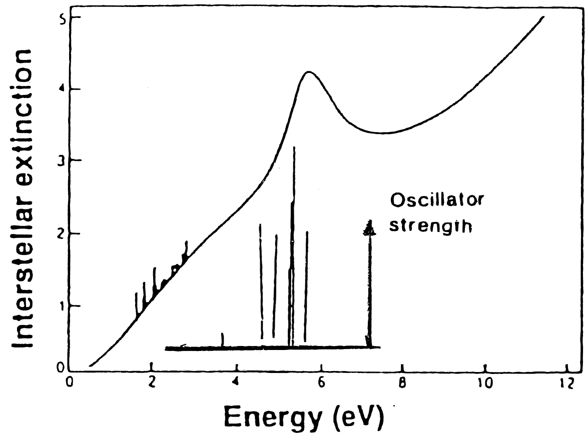

Figure 1. The interstellar extinction curve with the peak at 5.7 eV, 217 nm.[32] The interstellar bands[38] are shown around 2 eV in the extinction curve. Included are also evaluated oscillator strengths [39] of allowed transitions in C_{60}.

I got to know about C_{60} in connection with a meeting on clusters at Heidelberg in 1986,[37] where Smalley talked about C_{60} and its unique properties. The hope was that some of the diffuse interstellar bands by Herbig[38] as shown in Figure 1 might originate from transitions in C_{60}. Immediately after that meeting, I started calculations of C_{60} using density functional methods, but found that such methods were not appropriate to get reliable transition energies and oscillator strengths. My colleague Sven Larsson from the early 1960s, who had moved to Göteborg from Uppsala and Lund, joined me in using semi-empirical CI-methods for evaluation of the optical spectrum of C_{60}. The results of this work were published in 1987.[39] The calculations showed, in addition to a very weak transition at 340 nm (3.6 eV), a number of strong transitions in the UV around 214 nm (5.6 eV), as indicated in Figure 1.

The prediction of the weak transition was not so far from a transition at 386 nm (3.2 eV) observed by Smalley et al.[40] for C_{60} attached to $C_{60}H_6$ and $C_2H_2Cl_2$. At that time, we did not realize that this combination of strong transitions or *Finger Print* in the region around 5–6 eV would later help in the development of a method for producing macroscopic amounts of fullerenes. To further analyze the accuracy of the calculations, more extensive CI-calculations were done for C_{60} and its ions.[41,42] In the meantime, some density functional calculations were done for C_{60}, its ions[43] and for La@C_{60}.[44]

When investigating in 1987,[45] Huffman found that the predicted optical transitions in C_{60} fitted rather nicely, [39] although not perfectly, to the observed triple-humped structure or the "camel hump smoke" in the UV-visible spectrum. Furthermore, the observed Raman spectrum for this kind of unknown species of carbon was also in good agreement with vibrational calculations by Wu et al..[46] The agreement between both sets of experimental and theoretical data seems to have convinced

Huffman and Krätschmer that they had already produced C_{60} in 1983. All that was left to do was to purify and characterize the special carbon soot.

Krätschmer, Huffman, and students presented their new discoveries at a conference on Astrophysics held at Capri Italy in September 1989 and published their results in 1990.[47] At that time they suspected that the observed transitions in the IR might originate from oil in the diffusion pumps. Continued experiments[48] with samples enriched with ^{13}C compared with ^{12}C showed the expected shifts, which provided further proof that the characteristic absorption originated from the special carbon soot.

Krätschmer, Huffman et al. found later[49] that this special carbon soot could be dissolved in benzene, which provided the possibility to separate C_{60} from the carbon particles. The contribution from the background of carbon particles was thus eliminated and very strong absorption peaks at 216, 264, and 339 nm remained. This can be compared with the spectrum from the special carbon soot with the "the camel hump smoke" as shown in Figure 2.

The news spread that an extraordinary discovery had taken place in carbon research, which was a great occasion when compared with what had been known about clusters of carbon for a long time.[50,51]

Probably the first public announcement of the discovery was given as a short presentation by Krätschmer in connection with a talk by Smalley at the ISSPIC 5 conference at Konstanz, Sept 10–14, 1990.[52] This was only the beginning of research on carbon clusters, where the fullerenes were so unique and gave an almost epidemic spread of fullerene research.[53]

PERIODIC TABLE IN THREE DIMENSIONS

Today cluster science, and in particular the study of fullerenes and related carbon species, has developed into a very interdisciplinary area of science with a number of unique discoveries. A cluster can be characterized as an assembly of atoms or molecules that are bonded together in larger units. The term "metal atom cluster" seems to have been introduced by the chemist Cotton[54] to designate a finite group of metal atoms that are held together mainly, or at least to a significant extent, by bonds directly between metal atoms, even though some non-metal atoms may also be intimately associated with the cluster.[55,56]

Systematic studies of clusters can be seen as the exploration of the "The Periodic Table in a Third Dimension," as shown in Figure 3.

This figure gives an overview of the standard periodic table, where the first plane represents our knowledge of atoms and the second plane represents diatomic molecules.[57] Successive adding of atoms in a third dimension will give still larger clusters with the solids at the far end. Today we have a good knowledge of the species we start with, i.e., the atoms, diatomic molecules, and the end products, the solids,[58] while the knowledge of the species between the clusters, is growing. This is particularly true for carbon clusters.

SERENDIPITY AND SCIENTIFIC PROGRESS

In retrospect, it is interesting that indications of such unique species existed before without being noticed by researchers (Figure 4). In general, it seems that many people are so focused on a given problem that they do not realize that major discoveries or serendipities may exist in the results obtained. As discussed by Jim Baggot, this reduces to the role of scientific progress.[60] An example is the paper published by Iijima in 1987,[51] where he discusses how "when he found the article by Kroto et al.[22] was reminded about a 6-year-old work on electron microscopic observation of carbon particles in the form of concentric shells." This observation was, however, of minor interest compared with what would appear within a few years.

In 1991, Iijima[61] found that when using the electric arc discharge evaporation method of Krätschmer and Huffman, some special form of "needle like species" was produced on one of the electrodes. Electron microscopy studies revealed that each needle was built up of coaxial tubes of graphitic sheets, ranging in number from 2 up to about 50. These species, known today as Multi Wall Nano Tubes (MWNT), formed the birth of a new form of nanotechnology, which was totally unexpected. In fact, everyone who has used the electric arc evaporation method has had such species on the electrodes without knowing about it. A few years later, Iijima and Ichihashi[62] and Bethune et al.[63] independently found when doping one of the electrodes with some elements such as Fe and Co,

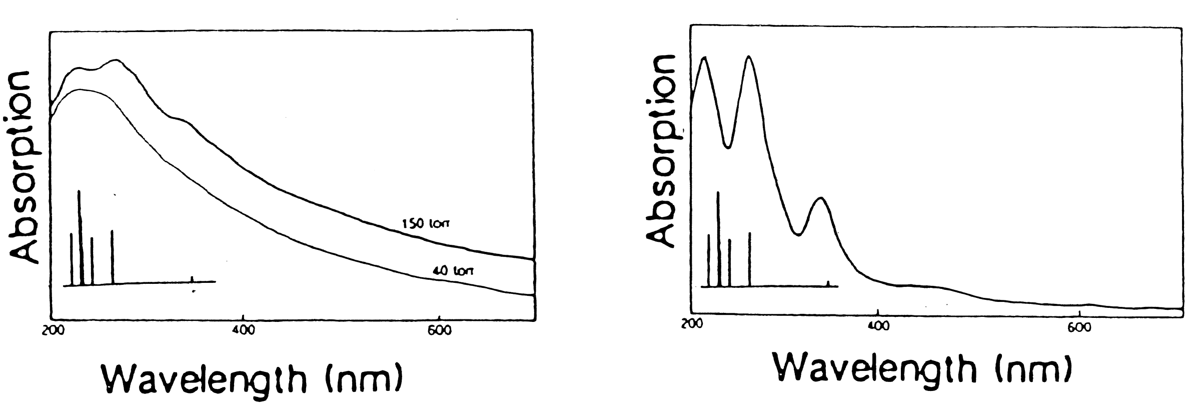

Figure 2. Absorption spectra for the special carbon soot to the left and C_{60} dissolved in benzene to the right. Our evaluation of the oscillator strengths [39] is included in both figures.

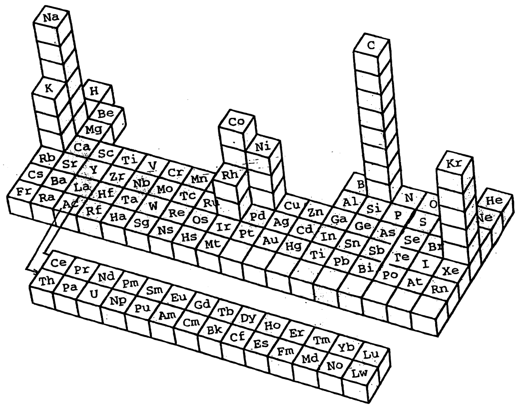

Figure 3. A schematic overview of how clusters built up from one element can be placed in a periodic table in three dimensions. In the case that the height in the third dimension will contain 6.023×10^{23} atoms we will have species corresponding to one mole of the element, approaching what is known for the solid.

Figure 4. Examples of how many scientists are so focused on certain problems that they do not realize how big discoveries in terms of serendipity would give scientific progress.[59] *Cartoon by Peter Schrank.*

that tubes with only one graphitic sheet known as Single Wall Nano Tubes (SWNT) were produced. About a year before that, Ugarte[64] found when studying fullerenes that increasing the current in the electron microscope produced a new type of structure in the form of Russian dolls known as carbon onions.

The research on fullerenes, MWNT, and SWNT has developed into a highly interdisciplinary field, which very few people could have imagined in the early 1990s.[65] It is particularly exciting how these new species have desirable characteristics for certain properties, which are comparable or even superior to materials used today. An example is the unique mechanical properties of nanotubes[66–68] with values of Young modulus, which are comparable or even superior with what is known for carbon fibers. Another example is the observation of

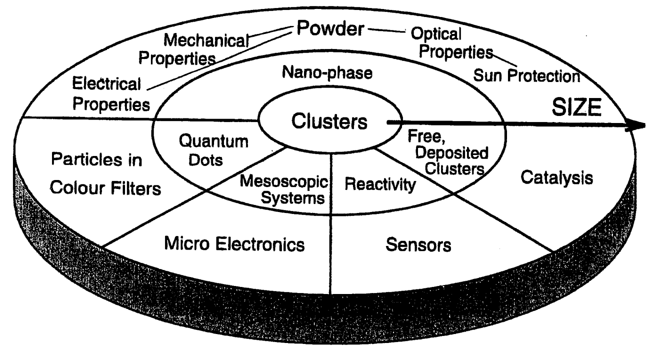

Figure 5. A schematic overview of how clusters are related to many areas of modern material science, micro electronics, and mesoscopic physics.

quantization of conductivity in nanotubes,[69–71] which has similarities to what is known for one-dimensional wires or a two-dimensional electron gas, 2DEG. Some years ago Reimann et al.[72] used the jellium model for large clusters to describe an experiment on the Aharaonov-Bohm effect for a 2DEG of GaAs. Recently, Batchold et al.[73] and Schönenberg et al.[74] have also observed the Aharaonov-Bohm effect for nanotubes.

Another unique feature is the interplay between experiments and theory where different kinds of theoretical methods have given important contributions to the development of the field. The whole field has been reviewed in a number of proceedings and books.[75–85] The remarkable properties of carbon nanotubes have recently been discussed in a special issue of Physics World,[86] which featured articles with the titles such as "Carbon nanotubes roll on," "Single-wall carbon nanotubes," "Multiwall carbon nanotubes," "Controlling nanotube growth," and "Industry sizes up nanotubes." The whole field of clusters, fullerenes, and, in particular, nanotubes will certainly a have big impact on the miniaturization at the nanometer scale.

OUTLOOK AND CONCLUSIONS

A sightseeing tour in the world of clusters with an extension of the periodic table in the third dimension has opened up a new area of science from the microscopic to the macroscopic world. When discussing modern nanotechnology it is rather common to refer to the visions of Richard Feynman. These visions were presented at a lecture for the American Physical Society at Caltec in 1959,[87] where he talked about the creation of new materials with new properties by manipulation of matter on a small scale. He presented the famous vision that he called "There's plenty of room at the bottom."

> "I would like to describe a field, in which little has been done, but in which an enormous amount can be done in principle. The field is not quite the same as others in that it will not tell us of fundamental physics (in the sense of "What are the strange particles ?"), but it is more like solid state physics in the sense that it might tell us much about the strange phenomena that occur in complex situations. Furthermore, a point that is most important is that it would have an enormous number of technical applications. What I want to talk about is the problem of manipulating and controlling things on a small scale. As

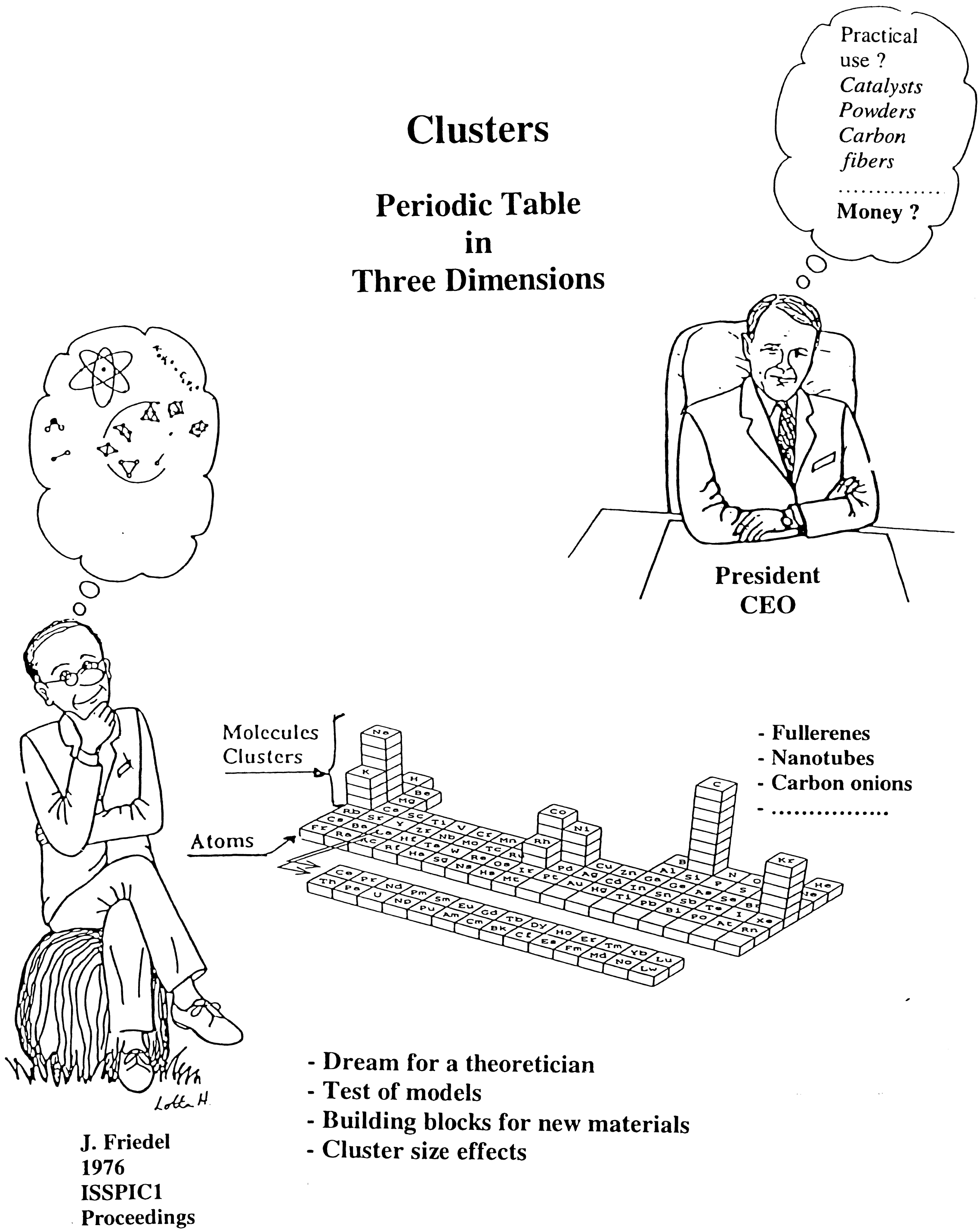

Figure 6. A schematic overview of clusters and the connection to basic research and practical applications as exemplified with a thinking scientist and the CEO for a company who has an interest in earning money. Cartoon by Lotta Holmgren.

soon as I mention this, people tell me about miniaturization, and how far it has progressed today. They tell me about motors that are the size of the nail on your small finger. And there's a device on the market, they tell me, by which you can write the Lord's Prayer on the head of a pin. But that's nothing; that's the most primitive, halting step in the direction I intend to discuss. It is a staggeringly small world that is below."

Feynman continues by discussing the visions of "How to write the Encyclopedia Britannica on the head of a pin." "Getting even smaller." "Rearranging atoms," and "Atoms in a small world," where he says:

> "When we get to the very, very small world-say circuits of seven atoms, we have a lot of new things that would happen that represent completely new opportunities for design. At-

oms on a small scale behave like nothing on a large scale, for they satisfy the laws of quantum mechanics. So as we go down and fiddle around with the atoms down there, we can expect to do different things. We can manufacture in different ways. We can use, not just circuits, but some system involving the quantized energy levels, or the interactions of quantized spins, etc. . . . At the atomic level, we have new kinds of forces and new kinds of possibilities, new kinds of effects. The problems of manufacture and reproduction of materials will be quite different. I am, as I said, inspired by the biological phenomena in which chemical forces are used in a repetitious fashion to produce all kinds of weird effects (one of which is the author)."

The visions given by Feynman have been fulfilled in many respects today, and even more has happened with the development of science into a highly interdisciplinary field. Particularly fascinating is how research in one area is of great use in other quite different areas of science. An example is the fabrication of an abacus of C_{60} molecules[88] with similarities to the earlier found quantum coralls.[89] These are just a few examples of how the visions of Feynman have been fulfilled, but it probably only represents the beginning of building new functional units in nanotechnology, as was done in the earlier "Stonehenge Era" when people used big stones as building blocks

Feynman was once asked the following question[90]: if you had only one sentence to pass on to the next generation the most important scientific knowledge we possess, what would that sentence be? Feynman's own answer was, "everything is made of atoms." *But what is there size and shape*, the next generation might reply, *and how do they stick together? Well*, Feynman might have said, *most scientists think of an atom as a sphere, like a tiny orange, and if you magnify an orange to the size of our Earth then every atom in the orange is magnified to the size of the original orange. But in reality, many atoms are not spherical and the shape of atoms critically affects how they bond together*. The unique character of carbon with the directional orientation of the 2p electrons and their hybridization with the 2s electrons are crucial for the formation of the different bonds in organic species. This was especially the case for the truncated icosahedral structure of 60 carbon atoms found in 1970 by Eji Osawa[24] and is also the case for all kinds of fullerenes, nanotubes, and carbon onions.

Particularly exciting from the basic science viewpoint has been the possibility to test models for species of a large number of fermions in the form of many thousands of atoms. We have adopted a numerically stable technique,[91] introduced by Salomonsson and Öster[92] in atomic calculations, to obtain the complete spectrum of occupied and unoccupied eigenstates of systems with cylindrical symmetry such as nanotubes and nanowires. The calculations are based on ab initio density functional formalism. Applying this technique to such systems with extreme spatial variations of the charge density, the electronic structure arising from the interacting 2*s* and 2*p* valence electrons of carbon are replaced by the point charges of the individual C^{4+} ions in the graphitic walls by two-dimensional charged "sheets" ("2D jellium background") of cylindrical symmetry, with uniform surface-charge density σ. For a graphitic honeycomb lattice with a C—C bond length of 2.68 a.u., we obtain $\sigma = +0.428$ e/a.u.^{2}. The same formalism can also be applied to nanowires. These calculations for nanotubes give electronic density of states with a quantization, which is similar to what is obtained in mesoscopic systems.

The species discussed in this article have established a connection between macroscopic and mesoscopic physics, and have also formed a link between the microscopic world and the world described using classical mechanics (see Figure 5). Clusters containing large numbers of atoms also have connection with materials used in commercial applications such as powder technology, catalysts, sensors, microelectronics, etc.

The wish expressed by J. Friedel, "Access to free clusters is a dream for a theoretician,"[93] has, in some respects, been fulfilled in areas he never envisaged, although there is still a great deal of information missing, such as the geometrical structure for most of the clusters with the exception of the diatomics (see Figure 6). The Chief Executive Officer (CEO) of a company may therefore be pleased with the present status of the field of cluster science, fullerenes, and nanotubes. He knows, for example, how important the material properties of small particles are for production of hard materials. He might therefore hope to use nanoparticles with "tuned properties" to fabricate materials with improved properties compared with existing ones. Other examples are the production of single and multiwalled nanotubes of controlled sizes for which the electronic behavior depends on the chirality of the tube.

As discussed above, nanotubes have also been found to have high values of Young modulus, comparable with what is known for carbon fibers. The CEO knows that carbon fibers are commercial products and therefore he or she might hope for new, improved materials in this area.

It might be appropriate to end this article with the words of Donald Huffman,[94] who has ended many lectures with the words, "Everything hasn't been discovered yet." A number of serendipities and unique discoveries will certainly show up in the areas of clusters, fullerenes, and nanotubes during the 21st century.

ACKNOWLEDGEMENT

Financial support from, NFR, The Swedish Natural Science Research Council (contract F–FU 2560–167), is gratefully acknowledged.

REFERENCES

1 *Clusters of Atoms and Molecules I and II.* Haberland H., Ed., Springer-Verlag, Berlin and Heidelberg, 1994
2 International Symposium on Small Particles and Inorganic Clusters (ISSPIC), Proceedings of ISSPIC conference 1 (ISSPIC 1), *J. Phys.* 1977, **38**
3 International Symposium on Small Particles and Inorganic Clusters, ISSPIC 2, *Surf. Sci.* 1981, **106,** 1–106
4 International Symposium on Small Particles and Inorganic Clusters, ISSPIC 3, *Surf. Sci.* 1985, **156,** 1–1071
5 International Symposium on Small Particles and Inorganic Clusters, ISSPIC 4, *Z. Phys. D.* 1989, **12,** 1–607
6 International Symposium on Small Particles and Inorganic Clusters, ISSPIC 5, *Z. Phys. D.* 1991, **D19,** 1–449, **D20** 1–467
7 International Symposium on Small Particles and Inorganic Clusters, ISSPIC 6, *Z. Phys. D.* 1993, **D26,** 1–396, **D26S,** 1
8 International Symposium on Small Particles and Inorganic Clusters, ISSPIC 7, *Surface Review and Letters.* 1996, **3,** 1–1226

9 International Symposium on Small Particles and Inorganic Clusters, ISSPIC 8, *Z. Phys. D.* 1997, **40,** 1–578
10 International Symposium on Small Particles and Inorganic Clusters, ISSPIC 9, *European J. Phys. D.* 2000, **9,** 1–651
11 deHeer, W.A. The physics of simple metal clusters: experimental aspects and simple models. *Rev. Mod. Phys.* 1993, **65**, 611
12 Brack, M. The physics of simple metal clusters: self-consistent jellium model and semiclassical approaches. *Rev. Mod. Phys.* 1993, **65**, 677
13 Echt, O., Sattler, K., and Recknagel, E. Magic numbers for sphere packings: experimental verification for free xenon clusters. *Phys. Rev. Lett.* 1981, **47**, 1121
14 Knight, W.D., Clemenger, K., deHeer, W.A., Saunders, W.A., Chou, M.Y., and Cohen, M.L. Electronic shell structure and abundances of sodium clusters. *Phys. Rev. Lett.* 1984, **52**, 2141
15 Ekardt, W. Work function of small spherical metal particles: Self-consistent spherical jellium-background model. *Phys. Rev.* 1984, **B29**, 1558
16 deHeer, W.A., Knight, W.D., Chou, M.Y., and Cohen, M.L. Electronic shell structure and metal clusters. *Solid State Physics.* 1987, **40**, 93
17 Pedersen, J., Bjornholm, S., Borggreen, J., Hansen, K., Martin, T.P., and Rasmussen, H.D. Observation of quantum supershells in clusters of sodium atoms. *Nature.* 1991, **353**, 733
18 Martin, T.P., Bjornholm, S., Borggreen, J., Brechignac, C., Cahuzac, Ph., Hansen, K., and Pedersen, J. Electronic shell structure of laser-warmed Na clusters. *Chem. Phys. Lett.* 1991, **186**, 53
19 Martin, T.P., Bergmann, Gohlich, T.H., and Lange, T. Observation of electronic shells and shells of atoms in large Na clusters. *Chem. Phys. Lett.* 1991, **172**, 209
20 Engineering a small world: from atomic manipulation to microfabrication, Special section in *Science.* 1991, **254**
21 Rohrer, H. Limits and Possibilities of Miniaturization. *Jpn. J. Appl. Phys.*,**32**, 1335 (1993)
22 Kroto, H.W., Heath, J.R., O'Brien, S.C., Curl, R.F., and Smalley, R.E. C_{60}: Buckminsterfullerene. *Nature.* (1985), **318**, 162
23 Rosén, A., and Wästberg, B. Buckminsterfullerene C_{60}—a surface with curvature and interesting properties. *Surf. Sci.* 1992, **1970**, 1121
24 Osawa, E. *Kagaku (Kyoto)*, **25**, 854
25 Yoshida, Z., and Osawa, E. Aromaticity (Kagakudojin, Kyoto, 1971), 174—178
26 Rohlfing, E.A., Cox, D.M., Kaldor, A. Production and characterization of supersonic carbon cluster beams. *J. Chem. Phys.* 1984, **81**, 3322
27 Bloomfield, L.A, Geusic, M.E., Freeman, R.R., and Brown, L.W. Negative and positive cluster ions of carbon and silicon. *Chem. Phys. Lett.* 1985, **121**, 33
28 Hopkins, J.B., Landgridge-Smith, P.R.R., Morse, M.D., and Smalley, R.E. Supersonic metal cluster beams of refractory metals: Special investigations of ultracold Mo_2. *J. Chem. Phys.* 1984, **78**, 1267
29 Huffman, D. R., and Krätschmer, W. How we found it. *Mater. Res. Soc. Symp.* 1991, **206**, 601
30 Huffman, D.R. SOLID C_{60}. The discovery of a method for producing the soccer-ball-shaped buckminsterfullerene molecule in macroscopic abundance led to the discovery of a totally new form of crystalline carbon. *Physics Today.* 1991, **Nov 91**, 22
31 Huffman, D.R., and Krätschmer, W. Private communication
32 Huffman, D.R. Interstellar grains. The interaction of light with a small particle system. *Adv. Phys.* 1977, **26**, 129
33 Stecher, T.P. Interstellar extinction in the ultraviolet. II. *Astrophys. J.* 1969, **157**, L125
34 Purcel, E.M., and Pennypacker, C.R. Scattering and absorption of light by nonspherical dielectric grains. *Astrophys. J.* 1973, **186**, 705
35 Klucker, R., Skibowski, M., and Steinmann, W. Anisotrophy in the optical transitions from the π and σ valence bands of graphite[1]. *Phys. Stat. Sol.* 1974, **65**, 703
36 Day, K.L., and Huffman, D.R. Measured extinction efficiency of graphite smoke in the region 1200-6000 A. *Nature, Phys. Sci.* 1973, **243**, 50
37 *Metal Clusters.* Träger, F., and zu Putlitz, G., Eds., *Z. Phys. D.* 1986, **3,** 103
38 Herbig, E. Famous review of the Diffuse Interstellar Line problem. *Astrophys. J.* 1975, **196**, 129
39 Larsson, S., Volosov, A., and Rosén, A. Optical spectrum of the icosahedral C_{60}—"follene-60." *Chem. Phys. Lett.* 1987, **137**, 501
40 Heath, J.R., Curl, R.F., and Smalley, R.E. The UV absortion spctrum of C_{60} (Buckminsterfullerene): A narrow band at 3860 Å. *J. Chem. Phys.* 1987, **87**, 4326
41 Braga, M., Larsson. S., Rosén. A., and Volosov, A. Electronic transitions in C_{60}. On the origin of the strong interstellar absorption at 217 nm. *Astron. Astrophys.* 1991, **245**, 232
42 Braga, M., Rosén, A., and Larsson, S. Electronic transitions in C_{60} and its ions. *Z Phys.* 1991, **D19,** 435
43 Rosén, A., and Wästberg, B. Calculations of the ionization thresholds and electron affinities of the neutral, positively and negatively charged C_{60} — "follene-60." *J. Chem. Phys.* 1989, **90**, 2525
44 Rosén, A., and Wästberg, B. First-principle calculations of the ionization potentials and electron affinities of the spheroidal molecules C_{60} and LaC_{60}. *J. Amer. Chem. Soc.* 1988, **110**, 8701
45 Huffman, D.R., and Krätschmer, W. Personal communication
46 Wu, Z.C., Jelski, D.A., and George, T.F. Vibrational motions of buckminsterfullerene. *Chem. Phys. Lett.* 1987, **137**, 291
47 Krätschmer, W., Fostiropoulos, K., and Huffman, D.R. Search for the UV and IR spectra of C_{60} in laboratory produced carbon dust. In: *Dusty Objects in the Universe*, Bussoletti, E., and Vittine, A.A., Eds., Kluwer Academic Publishers, Dordrect, Boston London, 1988
48 Krätschmer, W., Fostiropoulos, K., and Huffman, D.R. The infrared and ultraviolet absorption spectra of laboratory-produced carbon dust: evidence for the presence of the C_{60} molecule. *Chem. Phys. Lett.* 1990, **170**, 167
49 Krätschmer, W., Lamb, L.D., Fostiropoulos, K., and Huffman, D.R. Solid C_{60}: a new form of carbon. *Nature.* 1990, **347**, 354
50 Palmer, H., and Shelef, M. *Chemistry and Physics of Carbon* **4**, 85 Walker Jr, J.R., Ed., Marcel Dekker, New York 1967
51 Weltner, W., and Van Zee, R.J. Carbon molecules, ions and clusters. *Chem. Rev.* 1990, **89**, 1713

52 Krätschmer, W., How we came to produce the C_{60} -fullerite. *Z. Phys.* 1991, **D19**, 405
53 Braun, T. The epidemic spread of fullerene research. *Angew. Chem. Int. Ed. Engl.* 1992, **31**, 588
54 Cotton, F.A., Metal atom clusters in oxide systems. *Inorg. Chem.* 1964, **3**, 1217
55 Cotton, F.A. *Quart. Rev. 1966*, **20**, 389
56 Cotton, F.A. *McGraw-Hill Yearbook of Science and Technology*. McGraw-Hill, New York, 1966
57 Huber, K.P., and Herzberg, G. *Molecular Spectra and Molecular Structure, Constants of Diatomic Molecules.* van Nostrand Reinhold Comp, New York, 1979
58 Ashcroft, N.W., and Mermin, N.D. *Solid State Physics.* Saunders College, CBS Publ. Asia Ltd., Philadelphia, 1976
59 Baggott, J. Perfect symmetry: The accidential discovery of buckminsterfullerene. *New Scientist* 1990, **March 3**
60 Iijima, S. The 60-carbon cluster has been revealed! *J. Phys. Chem.* 1987, **91**, 3466
61 Iijima, S. Helical microtubules of graphitic carbon. *Nature.* 1991, **354**, 56
62 Iijima, S., and Ichihashi, T. Single-shell carbon nanotubes of 1-nm diameter. *Nature.* 1993, **363**, 603
63 Bethune, D.S., Klang, C.H., de Vries, M.S., Gorman, G., Savoy, R., Vasquez, J., and Beyers, R. Cobalt-catalysed growth of carbon nanotubes with single-atomic-layer walls. *Nature.* 1993, **363**, 605
64 Ugarte, D., Curling and closure of graphitic networks under electron-beam irradiation. *Nature* 1993, **359**, 707
65 Braun, T., Schubert, A.P., and Kostoff, N. Growth and trends of fullerene research as reflected in its journal literature. *Chem. Rev.* 2000, **100**, 23
66 Treacy, M.M.J., Ebbesen, T.W., and Gibson, J.M. *Nature.* 1996, **381**, 678
67 Wong, E.W., Sheehan, P.E., and Lieber, C. Nanobeam mechanics: elasticity, strength, and toughness of nanorods and nanotubes. *Science.* 1997, **277**, 1971
68 Yu, M-F., Lourie, O., Dyer, M.J., Moloni, K., Kelly, T.F., and Ruoff, R.S. *Science* 2000, **287**, 637
69 Tans, S.J., Devort, M.H., Dai, H., Thess, A., Smalley, R.E., Geerligs, L.J., and Dekker, C. *Nature.* 1997, **386**, 474
70 Wilder, J.W.G., Venema, L.C., Rinzler, A.G., Smalley, R.E., and Dekker, C. *Nature.* 1998, **391**, 59
71 Dekker, C. Carbon nanotubes as molecular quantum wires. *Physics Today*. 1999, **May**, 22–28
72 Reimann, S.M., Brack, M., Magner, A.G., and Murphy, M.V.N. Applications of classical periodic orbit theory to circular billiards with small scattering centers. *Surf. Rev. Lett.* 1996, **3**, 19
73 Bachtold, A., Strunk, C., Salvetat, J.-P., Bonard, J.-M., Forró, L., Nussbaumer, T., and Schönenberger, C. Aharonov-Bohm oscillations in carbon nanotubes. *Nature.* 1999, **397**, 673
74 Schönenberger, C., Bachtold, A., Strunk, C., Salvetat, J.-P., and Forró, L. Interference and Interaction in multiwall carbon nanotubes. *Appl. Phys.* 1999, **A69**, 283
75 Fullerenes, synthesis, properties and chemistry of large carbon clusters. *Am. Chem. Soc. Symp.* 1992, **481**, Hammond, G.S., and Kuck, V.J., Eds.
76 Special Issue on Buckminsterfullerene. *Acc. Chem. Research.* 1992, **25**, Eds. McLafferty, F.W.
77 Kroto. H.W. C_{60}: Buckminsterfullerene, The celestial sphere that fell to earth, *Angew. Chem.* 1992, **31**, 111
78 Special Issue on Fullerenes *Carbon.* 1992,**30**, 1139—1277 Kroto, H., 1992, Pergamon Press, New York
79 Physics and chemsitry of fullerene-based solids. *J. Phys. Chem. Solids.* **53**, 1992, Fischer, J.E., and Cox, D.E., Eds., Pergamon Press, New York
80 Renschler, C.L., Pouch, J.J., and Cox, D.M., Eds., Novel Forms of Carbon. *Mater. Res. Soc. Symp.* **270**
81 Clusters and fullerenes, Proc. Adriatico. Res. Conf., *Int. J. Mod Phys.* **B6**, 1992, Kumar, V., Martin, T.P., and Tosatti, E., Eds., World Scientific, Singapore
82 *Solid State Physics.* **48**, 226, Ehrenreich, H., and Spaepen, F., Eds., Academic Press, Boston, 1994
83 *The Chemical Physics of Fullerenes 10 (and 5) Years Later*, Natos. ASI Series E: Applied Sciences, Vol. 316, Andreoni, W., Ed., Kluwer Acad. Publ.
84 Dresselhaus, M.S., Dresselhaus, G, and Eklund, P. C. *Science of Fullerenes and Carbon Nanotubes.* Academic Press, San Diego, 1996
85 *The Science and Technology of Carbon Nanotubes.* Tanaka, K., Yamabe, T., and Fukui, K., Eds., Elsevier, Amsterdam, 1999
86 Carbon nanotubes: strengths, weakness, opportunities and challenges. *Physics World Special issue.* 2000, **13, 6**
87 Feynman, R. The man who dared to think small. *Science* 1991, **254**, 1300
88 Cuberes, M. T., Schlittler, R.R., and Gimzewski, J.K. Room-temperature repositioning of individual C_{60} molecules at Cu steps: Operation of a molecular counting device. *Appl. Phys. Lett.* 1996, **69**, 3016
89 Crommie, M.F., Lutz, C.P., and Eigler, D.M. Confinement of electrons to quantum corrals on a metal surface. *Science.* 1993, **262**, 218
90 Humphreys, C.J. Electrons seen in orbit. *Nature.* 1999, **401**, 21
91 Östling, D., Tománek, D., and Rosén, A. Electronic structure of single-wall, multiwall, and filled carbon nanotubes. *Phys. Rev.* 1997, **B55**, 13980
92 Salomonson, S., and Öster, P. Solution of the pair equation using a finite discrete spectrum. *Phys. Rev.* 1989, **A40** , 5559
93 Friedel, J., International Symposium on Small Particles and Inorganic Clusters (ISSPIC), Proceedings of ISSPIC conference 1 (ISSPIC 1), *J. Phys.* 1977, **38**,
94 Huffman, D.R. Ten years of teaching with fullerenes. *Electrochemical Society* 2000, **2000-1**, Abstract No. 647