Development of computational algorithms for the generation of graphene based structures

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Abstract

GAMGI is a free program available for Linux operating systems, used for the construction, visualization and analysis of atomic structures.

The objective of this work was the research, development and implementation in GAMGI of algorithms that allow the creation of molecular structures based on graphene: nanotubes, nanocones and fullerenes.

Graphene is a carbon based structure which presents interesting mechanical, thermal and optical properties. Three important classes of atomic structures may be computationally generated from graphene: carbon nanotubes, carbon nanocones and fullerenes. These molecules, like graphene, present properties that make them interesting for applications in different scientific areas, such as medicine and engineering.

Algorithms were developed and implemented throughout the course of this work, which allow for the generation of any single-walled nanotube of the zig-zag, armchair and chiral types, with an arbitrary height. Other algorithms were equally developed and implemented which allow for 16 kinds of open or closed nanocones to be built, with an arbitrary height, with disclination angles between 60° and 300°, differing in the positions or only locally, as a result of the applied construction method. Finally, caps were built which, when correctly applied to specific classes of nanotubes – (5,0), (5,5) and (6,6) – allow for the generation of infinite series of fullerenes, which include the most experimentally observed molecules of this type, C_{60} and C_{70}, in both cases with the 12 pentagons (demanded for this kind of structure) all isolated.

Key-words: graphene, carbon, nanotubes, nanocones, fullerenes, algorithms

1 Introduction

This work was elaborated with the objective of creating additional functionalities to the free and open-source program GAMGI (General Atomistic Modelling Interface) [1]. The goal of this program, as stated on the official website, is "… to provide a free package to construct, view and analyze atomic structures, as powerful and simple to use as possible". At the beginning of this work, GAMGI lacked the functionality of directly creating any kinds of molecules from simple input parameters given by the user. Over the course of this work, code has been written and added to the program, which allows for the creation of several different graphene based structures, namely carbon nanotubes, carbon nanocones and fullerenes. Algorithms that create the molecules based on user input were researched and then implemented in C code, after which they were subject to continuous development. The graphical interface also suffered various modifications to adjust to the new functionalities, so as to allow for direct user input.

2 State of the art

In 2010, the Nobel Prize in Physics was awarded jointly to Andre Geim and Konstantin Novoselov "for groundbreaking experiments regarding two-dimensional material graphene". Graphene (Figure 1) is an outstanding material due to its mechanical, electrical, thermal and optical properties [2], [3], [4]. It holds great promise in terms of its applications, the most attractive being within the area of material/device applications, such as solar cells, LEDs, touch panels and smart windows or phones [5]. Graphene is a crystalline allotrope of other important carbon structures with 2-dimensional properties, such as carbon nanotubes, fullerenes and nanocones. These structures inherit some of the properties of graphene, so it is also very interesting to study them.
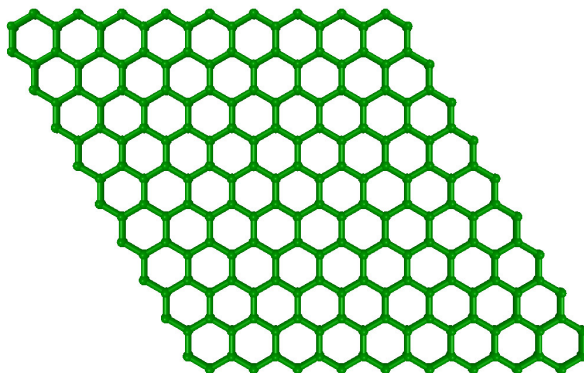

Figure 1 - The graphene honeycomb lattice

Carbon nanotubes are allotropes of carbon with a cylindrical shape. They can be thought of as rolled up sheets of graphene. There are several ways in which the sheet can be rolled to form a nanotube, and depending on that, the nanotube will exhibit different properties, such as whether it is metallic or

semiconductor [6]. Carbon nanocones are conical structures which are made predominantly from carbon and which have at least one dimension of the order one micrometer or smaller [7]. There are also several ways in which the sheet can be rolled to form a nanocone, and they will also influence the properties. Fullerenes are closed carbon-cage molecules containing only pentagonal and hexagonal rings, where every atom has bonds with exactly 3 other atoms, idealized as sp^2 hybridized atoms [8]. All of these molecules show great promise in different scientific and engineering areas, and are already being applied, namely carbon nanotubes as reinforcement material [9], carbon nanocones as scanning probe tips and electron field emitters [10], [11], and fullerenes various medical fields [12], [13]. Fullerenes in particular have also attracted the interest of the scientific community in the area of graph theory, where scientists have studied and developed algorithms to try to create all possible fullerene isomers [14].

3 Algorithms and Results

The algorithms were based and developed upon pre-existing scientific works, and implemented in the C programming language. The source code, totalling a number of 2356 lines, is divided among six files.

3.1 Graphene

Before explaining the generation algorithms for nanotubes, nanocones and fullerenes, it is important to know how to generate graphene. Graphene can be described by a 2D hexagonal lattice with vectors $\mathbf{a_1}$ = a.$\mathbf{x}$ and $\mathbf{a_2}$ = a.sin (120º).$\mathbf{x}$ + a.cos (120º).$\mathbf{y}$, with carbon atoms at positions (0, 0) (A atoms) and (2/3, 1/3) (B atoms). The lattice parameter a = 2.467 Å is thus simply related with the CC bond distance between the two atoms: $a = bond * \sqrt{3}$.

3.2 Nanotubes

Nanotubes are, like graphene, described by two base vectors, separated by a 60º angle: $\mathbf{b_1}$ = a.$\mathbf{x}$ and $\mathbf{b_2}$ = a.sin (60º).$\mathbf{x}$ + a.cos (60º).$\mathbf{y}$. Since the lattice is hexagonal, these vectors are also lattice vectors. Any (m,n) integer combination of these two vectors represents a translation vector $\mathbf{T}$ of the lattice, which links two equivalent points:

$$T = m \cdot \boldsymbol{b_1} + n \cdot \boldsymbol{b_1}$$

Two lines perpendicular to $\mathbf{T}$ passing through these two equivalent points, must also be equivalent, allowing us to define a rectangle with length |$\mathbf{T}$| and equivalent sides of height h, as shown in Figure 2. As the two sides are equivalent, the rectangle can folded and the two sides linked, forming a perfect seam, thus forming the final nanotube structure.
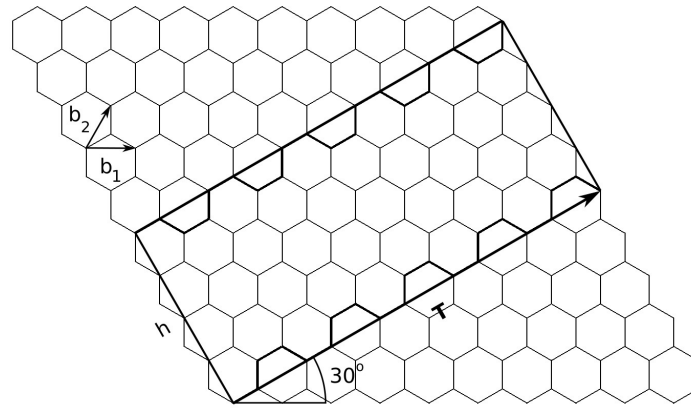
Figure 2 - Selection rectangle for a (5,5) carbon nanotube. T is the translation vector, b1 and b2 the nanotube base vectors, and h is the height

The integer coordinates (m,n) uniquely identify the whole atomic structure of a nanotube, including its radius and, most importantly, its type. An (m,0) nanotube is called a zig-zag, an (m,m) nanotube is called an armchair and an (m,n) nanotube is called a chiral, these names being attributed based on the top and bottom outlines of the nanotube, each of which makes a different angle θ with the horizontal **x** axis.

To select the atoms within the 2D rectangle, vectors $\mathbf{a_1}$ and $\mathbf{a_2}$ are first rotated of the angle $-\theta$, together with the rectangle. The atoms inside the transformed, horizontal, rectangle are selected by checking whether the x coordinate is between 0 and T (the length of the vector **T**) and the y coordinate is between 0 and h.

The range of hexagonal graphene cells that must be considered to include all the relevant atoms must be a lozenge which fully covers a semi-circular area of radius r, where r is the length of the diagonal of the rectangle.

To convert the 2D rectangle of atoms into the 3D nanotube, we notice that the rectangle length T is simply the perimeter of the nanotube, so the nanotube radius (unrelated to the previous one) becomes r = T / 2π. The 3D atom coordinates are then obtained applying the following transformation to all the atoms inside the 2D rectangle:

$$(x,y) \rightarrow (r \cdot \cos(\alpha), r \cdot \sin(\alpha), y)$$

with: $\alpha = 2\pi \cdot x/T$.

Atoms with x = T are superimposed over atoms with x = 0, so they must be discarded. This corresponds to, in terms of the primitive hexagonal lattice, that atoms at cells (i,j) are superimposed over atoms at cells (i,j) – **T.** If we write the nanotube translation vector as an integer combination of the graphene base vectors:

$$\boldsymbol{T} = (m+n) \cdot \boldsymbol{a_1} + n \cdot \boldsymbol{a_2}$$

it is easy to see that an atom at a cell (i, j) must be discarded if another atom has been previously alocated in a lower cell (i - m - n, j – n).

The final step in generating nanotubes is to create the bonds between the atoms. Through direct inspection, it can be seen that each atom A in a cell (i, j) should be connected to 3 atoms B at cells (i, j), (i – 1, j) and (i – 1, j – 1), and this is enough to create local bonds. To create the bonds between atoms at opposite borders of the rectangle (atoms that form the seam region), the periodic boundary conditions must be applied. Therefore, the general procedure to create the nanotube bonds is: for each atom A in a cell (i, j), try to find an atom B in cells (i, j), (i – 1, j) and (i – 1, j – 1) (local atoms) or in cells (i + m + n, j + n), (i + m + n – 1, j + n) and (i + m + n – 1, j + n – 1) (atoms close to the left border: α → 0, applying **+T** periodic boundary conditions) or in cells (i – m – n, j – n), (i – m – n – 1, j – n) and (i - m - n - 1, j - n – 1) (atoms close to the right border: α → 2π, applying **+T** periodic boundary conditions). For a better understanding, see Figure 3.
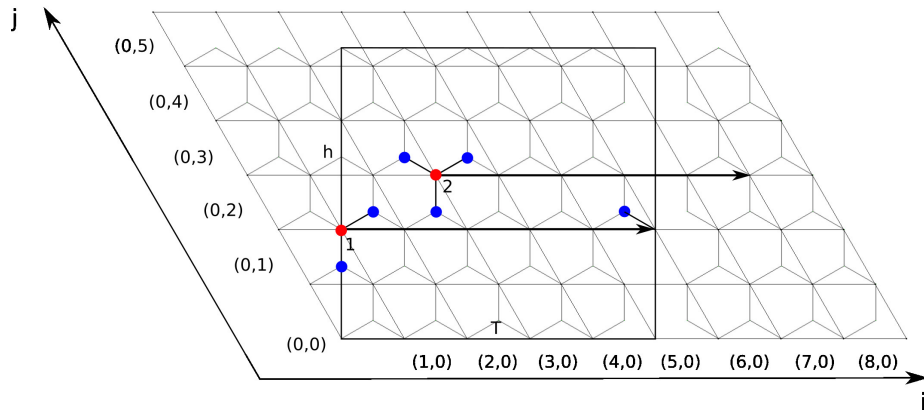

Figure 3 - Nanotube bonding scheme. Atom 1 makes 2 local bonds and one associated with periodic boundary conditions. Atom 2 only makes local bonds

The incorporation of these algorithms in GAMGI allows for the creation of nanotubes, like the ones seen in Figure 4:
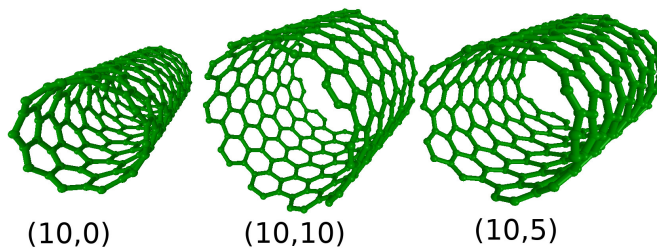

Figure 4 -The (10,0), (10,10) and (10,5) nanotubes

3.3 Nanocones

As in the case of carbon nanotubes, a graphene sheet is used to create carbon nanocones. In this case, however, we want the initial 2D sheet to be circular, in the simpler cases with the origin at the center of a hexagon instead of an atom, so the two carbon atoms per graphene cell are at positions (2/3, 1/3) and (1/3, 2/3). Nanocones can be described by a disclination angle, Δ, which is the angle of the circular slice, starting from the circle center, that is removed before folding the sheet until the two slice borders are reunited again, forming a 3D nanocone. This angle Δ can have the value of 60°, 120°, 180°, 240° and 300°. Nanocones may be closed or open, in which case they lack the top part, or apex of the cone, so two radii are defined: the outer radius of the sheet (r_{out}) and the inner radius of the sheet (r_{in}). To select the atoms within the circular area that is left after cutting the slice corresponding to the disclination angle, it is necessary to check if their distance from the center is smaller than or equal to r_{out} and greater than or equal to r_{in}, and if the angle they make with the **x** axis is greater than the disclination (see Figure 5):
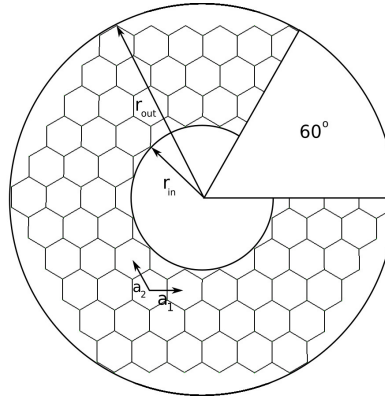

Figure 5 - The selection area for a nanocone is the circular crown with maximum and minimum radii rout
and rin, minus the 60° disclination gap

An exercise similar to the case of nanotubes is applied to find the range of graphene cells that must be considered in order to generate all the relevant atoms. In this case, range of hexagonal graphene cells that must be considered to include all the relevant atoms must be a lozenge which fully covers a circular area of radius r_{out}.

To convert the 2D circular slice of atoms into the 3D nanocone, one side of the slice remains fixed, while the other rotates an angle equal to -Δ, in order to fill the gap left from removing the area corresponding to the disclination. The value of the angle, α_{cone}, of an atom in the nanocone is calculated from its value in the graphene sheet, α_{sheet}, through the formula:

$$\alpha_{cone} = 2\pi\left(1 - \frac{2\pi - \alpha_{sheet}}{2\pi - \Delta}\right)$$

The 3D atom coordinates are then obtained applying the following transformation to all the atoms inside the circular slice area:

$$(x,y,z) \rightarrow (l \cdot f \cdot \cos(\alpha_{cone}), l \cdot f \cdot \sin(\alpha_{cone}), h \cdot (1 - \frac{l}{r_{out}}) - h/2)$$

where l is the distance of an atom from the center, f = r_{cone} / r_{out}, and h is the height of the nanocone.

For several partial disclinations of 60° each, acting together, the hexagons at which they are centered will be transformed into pentagons, as one of the six atoms of the original hexagon has been removed.. Depending on the center of the disclinations, different isomers of a nanocone with a specific total disclination may be generated, since the pentagons will be located at different places of the structure. Moreover, rotating only one end or both ends of the angular gaps left by disclinations produce different results. Therefore, several different isomers can be created for the same total disclination.

First, if the nanocone model so requires, the origin is changed so that it becomes the center of a bond. Then, the atoms with distance from the center greater than r_{out} or smaller then r_{in} are removed. The steps that follow are successively applied for each disclination, with the calculations being made as though a disclination is the origin of the cone. A check to see if the atoms lie outside the disclination area is made, with atoms being discarded if they are inside. Unlike in the case of a single disclination, not all atoms of the structure are rotated, so atoms that are not discarded are submitted to a final check which determines if they should be rotated in order to fill the vacant spots left by discarded atoms. This procedure becomes progressively more complex with the number of introduced disclinations.

To create bonds between atoms, a scheme similar to the one used for nanotubes can be applied. Considering the initial indices i and j of a 2D graphene sheet, each bond in a seam region (the region where the two loose edges come together through the bonding of the atoms) is always established between an A or B atom of an (i_0, j_0) cell on one side of the seam, and another A or B atom in an (i_1, j_1) cell on the other side of the seam. Also, if the atom on cell (i_0, j_0) is an atom A, then $k_0 = 0$, otherwise $k_0 = 1$. Identically, if the atom on cell (i_1, j_1) is an atom A, then $k_1 = 0$, otherwise $k_1 = 1$. It is necessary to determine one bond through direct inspection. This bond is chosen to be the one closest to the center of the nanocone. From this inspection, i_0, j_0, k_0, i_1, j_1 and k_1 are determined. Since the disclination area that is subtracted corresponds to a symmetry rotation, there is a natural, predictable progression of these indices. This progression must also be directly inspected, by determining 2 or 3 more bonds after the starting one. This progression can be identified by six other indices: ii_0, jj_0, kk_0, ii_1, jj_1, and kk_1, which are used in the algorithm. The bonding scheme for a single 60° with a bisector at 30° can be seen in Figure 6.
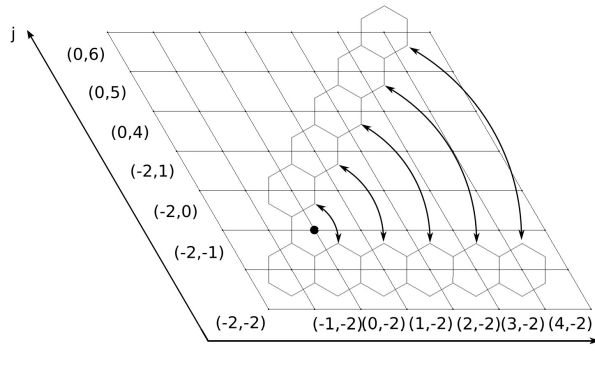
Figure 6 - Nanocone bonding scheme for a single 60° disclination between 0° and 60°

The incorporation of these algorithms in GAMGI allows for the creation of nanocones, like the one seen in Figure 7:
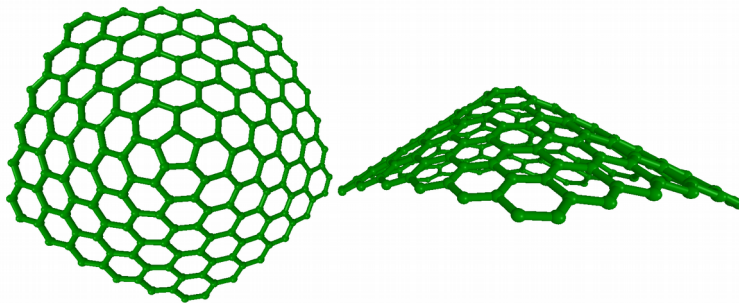

Figure 7 - Nanocone 60_O

3.4 Fullerenes

Hasheminezhad et al. presented three sets of patch replacement operations for fullerene graphs which allow the every fullerene graph, starting from C_{20} and C_{28}, to be generated, and these three sets of expansions are called L_i, $B_{i,j}$ and F. Among the three of them, F proves to be the most easily applicable one, since it simply consists in adding an hexagonal layer of rings around a structure composed of a central pentagon surrounded by five pentagons. Applying expansion F on C_{20} results in C_{30}, where a layer of five hexagonal rings is in between two "caps" composed of six pentagons. Applying expansion F on C_{30} results in C_{40}, and now the two caps are separated by two layers of five hexagonal rings. These fullerenes are no more than (5,0)-type nanotubes covered with caps, where the height of nanotube, given by the number of ring layers, corresponds to the application of expansion F to C_{20} as many times as the number of ring layers between the caps. Any combination of (m,n) fullerene nanotube can be created in this way, in particular the (5,5)- and (6,6)-types, with the shape of the caps being different in each case. By making use of the previously explained algorithms to generate nanotubes, all that remains is to cover the ends of

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the nanotube with a cap specific to the considered type of (m,n) nanotube, and this procedure is, compared to the the ones for nanotubes and nanocones, quite trivial. An image of C_{20} and the corresponding nanotube fullerene obtained from applying transformation F three times, C_{50}, can be seen in Figure 8:
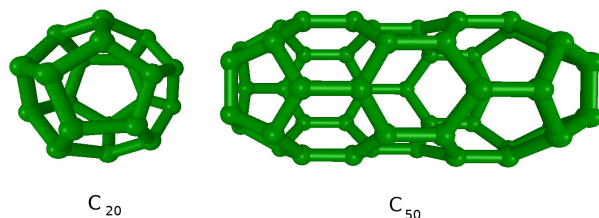

C_{20} C_{50}

Figure 8 - C_{20} and (5,0)-type nanotube C_{50}

Besides expansion F, a particular case of expansion L where i = 0 (L_0) and a special transformation that converts C_{28} to C_{24} (thus allowing every fullerene isomer to be generated from C_{20} alone) have been developed in this work. These transformations have successfully been implemented in code as far as creating bonds between atoms goes, but the atom positions are incorrect, so they have not been incorporated into GAMGI.

4 Graphical interface

Several features have been added to GAMGI's graphical interface that allow for the introduction of data by a user in order to produce any of the molecules that have been described in this work. If one chooses the option "Molecule" → "Create", it is now possible to choose, in the "Method" toolbox, to create graphene-based structures, namely sheets, nanotubes, nanocones, fullerenes (cages) and caps (Figure 9).
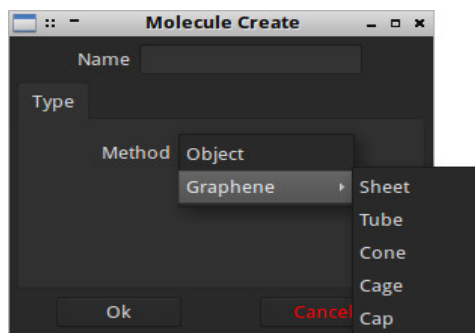

Figure 9 - Toolbox for the new "Molecule" -> "Create" option

5 Conclusion

With this work, new features have been added to GAMGI which allow for the creation of three types of graphene based structures: carbon nanotubes, carbon nanocones and fullerenes. GAMGI is now able to generate all kinds of nanotubes without restrictions, and with a good geometry. In the case of nanocones, the geometry of the more complex isomers that can be created can still be worked upon, and this can be achieved through the implementation of, for example, force-field methods. Finally, in what regards fullerenes, GAMGI can now generate fullerenes belonging to one of three different types of nanotubes. While this is certainly a good addition, GAMGI is not able to generate all the different fullerene isomers. To fill in this gap, research will have to be undertaken in the graph theory field, and the algorithms created by researchers will have to be thoroughly analyzed.

6 References

[1] "GAMGI - General Atomistic Modelling Graphic Interface." 30 Nov. 2016. http://www.gamgi.org/.

[2] Balandin, Alexander A. "Thermal properties of graphene and nanostructured carbon materials." *Nature materials* 10.8 (2011): 569-581.

[3] Apell, S. Peter, G. W. Hanson, and Carl Hägglund. "High optical absorption in graphene." *arXiv preprint arXiv:1201.3071* (2012).

[4] Chen, Jian-Hao, et al. "Intrinsic and extrinsic performance limits of graphene devices on SiO2." *Nature nanotechnology* 3.4 (2008): 206-209.

[5] Akinwande, Deji, et al. "Large-Area Graphene Electrodes: Using CVD to facilitate applications in commercial touchscreens, flexible nanoelectronics, and neural interfaces." *IEEE Nanotechnology Magazine* 9.3 (2015): 6-14.

[6] Lu, Xin, and Zhongfang Chen. "Curved pi-conjugation, aromaticity, and the related chemistry of small fullerenes." *Chemical Reviews* 105.10 (2005): 3643-3696.

[7] Ge, Maohui, and Klaus Sattler. "Observation of fullerene cones." *Chemical physics letters* 220.3-5 (1994): 192-196.

[8] Schwerdtfeger, Peter, Lukas N. Wirz, and James Avery. "The topology of fullerenes." *Wiley Interdisciplinary Reviews: Computational Molecular Science* 5.1 (2015): 96-145.

[9] "Pirahna USV built using nano-enhanced carbon prepreg". ReinforcedPlastics.com. 19 February 2009. Archived from the original on 3 March 2012.

[10] Lu, X., et al. "Field electron emission of carbon-based nanocone films." *Applied Physics A* 82.2 (2006): 293-296.

[11] Bonard, J-M., et al. "Field emission properties of carbon nanohorn films." *Journal of applied physics* 91.12 (2002): 10107-10109.

[12] Lalwani, Gaurav, and Balaji Sitharaman. "Multifunctional fullerene-and metallofullerene-based nanobiomaterials." *Nano Life* 3.03 (2013): 1342003.

[13] Bosi, Susanna, et al. "Fullerene derivatives: an attractive tool for biological applications." European journal of medicinal chemistry 38.11 (2003): 913-923.

[14] Brinkmann, Gunnar, Jan Goedgebeur, and Brendan D. McKay. "The generation of fullerenes." *Journal of chemical information and modeling* 52.11 (2012): 2910-2918.