A Topological approximation to the understanding of small metal clusters geometry

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Structural understanding of metal nanoparticles shape is made with the help of topological approximations, based on the topological evaluation of configurations. The mathematical formalism of the topology is used to establish the principles on which metallic atoms are arranged, and the form to generate classifications for the structures and observed surface morphologies. Metal nanoparticles can be determined as homeomorphous-like because their configuration and transformation rules. These mathematical principles allow the establishment of the significant facts that determine the particular set of geometries for low energy small metallic clusters.

Keywords: Nanoparticles; structure determination; topology principles; surface configuration; structural transformation; mathematical formalism.

La comprensión de la forma de nanopartículas metálicas es efectuada con ayuda de aproximaciones topológicas, basadas en la evaluación de configuraciones mediante bases matemáticas. El formalismo matemático de la topología es empleado para establecer los principios de arreglo de átomos metálicos, y la forma para generar clasificaciones para la morfología de las superfi cies producidas. Las nanopartículas metálicas pueden ser determinadas como del tipo homeomorfas debido a su configuración y las reglas de transformación que les rigen. Estos principios matemáticos permiten establecer importantes similitudes que son determinantes en la generación de un particular conjunto de geometrías para el caso de pequeños agregados metálicos de baja energía.

Descriptores: Nanopartículas; determinación estructural; principios de topología; configuración de superficie; trasformación de estructura; formalismo matemático.

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1. Introduction

Nanostructured materials have multiple perspectives in the near future, thanks to their unique properties [1-5]. Particularly the use of metal nanoparticles has important possibilities of being used in catalysis, [6] optical devices [7] and even medicine [8]; however the required properties are based on the quantum size effects, which are determined by the elemental composition, size and structure of the metal clusters [3-5,9-11].

Because of its importance, the structure determination has been an important goal for many researches, who have applied theoretical and experimental methods for the identification of the lowest energy (consequently the most probable) configuration of different types of structures and aggregates [9-13]. It has been demonstrated also that there is a dependence of the properties of the metal aggregates with the configuration, which can be associated to the presence of active sites, [5] the electronic configuration [11-12] and the own physicochemical affinity and selectivity [8].

For metal nanoparticles, it has been determined that polyhedral configurations mainly formed by the ordering of tetrahedrons generate cubic, icosahedron and decahedron clusters. [9,11,13] In fact the structure is established by the local interactions between atoms, which tend to reduce the surface energy. This behavior induces configurations such as the mentioned polyhedrons.

On the other hand, mathematics topology has been introduced for the understanding of multiple physical phenomena, as cosmology, [14] quantum mechanics [15] and several others, where the understanding of geometry and the corresponding effects are quite important. It is used also for the analysis of the configuration of polymers [16] and even a proposal can be found for using principles of topology for the characterization of materials [17]. However there is no report on the use of this topological approach to establish the conditions for the generation of shapes based on the aggregation of atoms, as in nanoparticles or nanometric structures. In this work, we are proposing a methodology to classify nanostructures based on a topological approach that could lead to a mechanism to predict morphologies and to understand structural transformations.

2. Topological preliminary statements

A non-empty, finite or infinite set $M$ of mathematical objects (called points) is denominated space of neighborhoods; if for
each point certain subsets can be defined, as its environments satisfy the following axioms:

**Axiom A**: For each point \( p \) of the space of neighborhoods \( M \), there is an environment at least; all neighborhood of \( p \) contains \( p \). We designate an neighborhood of \( p \) for \( U(p|M) \).

**Axiom B**: All subset of \( M \) that contains an neighborhood \( U(p|M) \) it is also an neighborhood of \( p \).

An application of a space of neighborhoods \( A \) in another space of neighborhoods \( B \) is determined *continuous* at a point \( p \) if for each neighborhood \( U(p'|B) \) of the image \( T(p) = p' \), there exists an neighborhood \( U(p|A) \) of \( p \) whose image belongs to \( U(p'|B) \). The application is called continuous, when it is continuous at any point.

A non singular application \( T \) of \( A \) on \( A' \) is called topological, when \( T \) and \( T^{-1} \) are continuous.

Two spaces of neighborhoods are called “homeomorphic” if can be applied one on another topologically.

We can divide the points of a space of environments \( M \) in classes (subsets) so that all point belongs to a class. The points of one class are called “equivalent points”. Let \( M' \) be the set of classes of equivalent points of \( M \). There exists a mapping of \( M \) on \( M' \) defined by the projection of each point of \( M \) in its corresponding equivalence class. \( M' \) becomes a space of environments with the next convention: If \( p_1, p_2, \ldots \) are all the points of \( M \) that are represented in oneself point \( p' \) of \( M' \), we choose, for each point \( p_i \) an neighborhood \( U(p_i|M) \) and apply in \( M' \), the image of \( U(p_1|M) \cup U(p_2|M) \ldots \) is defined as an environment \( U(p'|M') \) of \( p' \).

Such environments in \( M' \) satisfy the axioms A and B [18–20].

### 3. Structural parameters identification

**Definition 1.** A topological polygon is a circular disk of the plane \( \mathbb{R}^2 \) whose perimeter is divided in \( r \) (\( r > 2 \)) segments (called sides of the polygon) by means of \( r \) points called vertexes of the polygon. Also, it is polygon all the topological applications of that disc, translating to this image all the denominations of sides and vertexes.

**Definition 2.** A set \( M \) of topological polygons without common points in \( \mathbb{R}^2 \) whose sides are topologically applied to each other, is called a “polygonal system”.

Here we will consider just the polygonal systems where the total number of sides is even and each side is related to another with a topological application, because this involves the closed structures for atomistic arrays.

In a polygonal system \( \bar{M} \) the points of the polygonal system applied among them, produce equivalents points.

**Definition 3.** The set of points \( M \), resulting from the identification of equivalent points in \( M \) receives the name of “closed surface”, “closed manifold” or “polyhedron”. The adjective of closed means that the surface has a finite number of polygons and that there is no free edge.

In this way the points of a polygonal system applied between them produce different types of classes of equivalents points. It can be distinguished the next types of equivalents points in \( M \):

- a) A polygonal internal point is equivalent to itself;
- b) Interior points of a polygonal side, for each one there must exist exactly one equivalent point; and
- c) Vertexes. Which will have one, several or even none equivalent points.

Both, \( M \) and \( M' \) are spaces of environments. The interaction between polygonal sides can be produced randomly, just fulfilling the condition that polygons can not be divided into two types, which have sides interacting just between them (connectivity condition).

This corresponds to particles with low energy surface, establishing the nature of the clusters formation, which energetically is the most stable and geometrically establish the right topological properties.

**Definition 4.** The polygonal vertexes set belong to one equivalence class are transformed in a single point on the surface known as “vertex”. The amount of vertexes in a polyhedron, which match with the number of equivalence types are denoted as \( \alpha_0 \).

Similarly

**Definition 5.** The images of equivalents sides are named polyhedron edges and the corresponding polygons are called polyhedron faces. It is also established \( \alpha_1 \) and \( \alpha_2 \) for the number of edges and faces respectively.

Generally, both edges and sides will be continuous but no topological images for the polygonal sides and polygons. It can occur that the boundary points of a polygonal side are equivalent to a just one polyhedron vertex by the side’s correspondence. So the edge is on the surface of a topological circle. Similarly, the superficial faces can show self-contact along one or several edges, or even just one vertex. This is observed by instance in a polyhedron surface building using a single polygon, as for the “bull”, which is generated identifying opposite sides of a rectangle or even the Klein bottle.[18]

In a polygonal system the sides of each polygon are oriented with an arrow, such that in the application these sides match. The polygons are also oriented. The orientation of a polygon consists on guiding the entirety of its sides such as each vertex intervenes once as origin and another as end of the contiguous side. With the orientation of the polygons, the polygonal system can be indicated then purely by means of an outline combinatorial rule [21].

In order to interpret the polyhedron properties, we must separate three concepts:

- a) Polygonal system \( \bar{M} \), formed by disjoined polygons where certain points can be defined as equivalent.
- b) Polygonal surface \( \bar{M} \), which results from \( M \) when after identifying equivalent points, it is a surfaces with divided points in a specific way forming faces, edges and vertex.
c) Closed surface, generated by the polygonal system but it is no more needed such distribution.

It must be noticed that the vertex imply the presence of atoms in a metal nanoparticle, while the possible presence of more atoms aligned on the sides and internally on the faces would imply extra topological points. However for the general shape analysis, the shape of the faces are determined by the sides and consequently by the kind of interactions between atoms.

In this way polygonal sides can be considered to be oriented. It is determined one of the contour points of a side as its origin, making to match the corresponding sides focused to the origin application results in the same origin and the extreme into the same extreme. Also the polygons are oriented. This polygonal orientation process consists in the orientation of all the sides. The observed orientation for a side in the contour coherent orientation will be called induced orientation in that side from the polygonal one. Similarly, a polygon can be oriented in two different ways. Circular arrows inside the polygon indicate the orientation of each side and the corresponding to the full polygon.

Based on the polygonal orientation, it is established a path sense of their sides, a succession cyclic order for them. The polygonal system can be indicated then by means of a purely combinatorial scheme. Writing in different rows the sides of each one of the polygons, as are succeeded in a contour, following the given path sense and it will be considered as positive (+1 or with no marked) or negative (-1 or simply ') depending if the given orientation matches or is opposite to the induced orientation for the polygon. With this scheme, the polygonal system and consequently the surface are well determined. Each row will give the cyclic succession of the polygonal sides, the notation of the sides show the matching correspondence between these and the exponents will denote the way that the corresponding sides are topologically applied.

**Definition 6.** A subdivision of dimension one consist in divide two corresponding polygonal sides using a couple of corresponding points in each one of them, leaving with no changes the correspondence of the rest of the points. In the opposite way, the polygonal side sub-sectioned to the original is called “fusion of dimension one”.

**Definition 7.** A fusion of dimension two consist in joining two different polygons into just one, along the two identified equivalent sides. The inverse process, it means the decomposition of one polygon to produce two; it is named “sub-sectioning of dimension two”.

**Definition 8.** Two polygonal systems with the capability to transform one into the other by means of a finite number of sub-sectioning steps or fusions of order one or two are determined similarly to their polygonal surfaces “elementally related”.

Topologically, the determined surface for a polygonal system does not vary by a elemental transformation of dimension one, neither of dimension two (because the identification can be made step by step). That is the reason because we can establish that polygonal systems related elementally determine homeomorphic surfaces.

The polyhedral surfaces related elementally have two important properties, the Euler characteristic and the orientation capability:

**Definition 9.** The Euler characteristic of a polygonal system is based on the number N, which is associated to the number of edges, sides and faces of a polyhedron, where \( N = -\alpha_0 + \alpha_1 - \alpha_2 \).

**Theorem.** The polyhedral surfaces related elementally have the same Euler characteristic.

**Demonstration.** In fact, in an elemental transformation of dimension one, \( \alpha_0 \) and \( \alpha_1 \) vary in one unity remaining constant \( \alpha_2 \). Besides in a transformation of dimension two, \( \alpha_1 \) and \( \alpha_2 \) vary change in one unity each of them.

**Definition 10.** A polyhedral surface is orientable if its corresponding components of the polygonal system can be oriented in order to the corresponding sides appear with opposite induced orientations.

It can be determined that by means of sub-sections and fusions, the property of a polyhedral surface to have a orientation capability remains invariable.

### 4. Geometric analysis of metal structures configurations

The understanding of the different geometries distinguished to be the most stable for metallic particles are based on fcc-like and multiple twin structures mainly as octahedron and decahedron respectively. Besides to produced arrays with the growing of five fold system symmetrical and anti-symmetrical configurations known as Ino-decahedron and icosahedron. Also the forms based on the octahedron truncation, generating the called cuboctahedron and tetrakaidecahedron.[13]

Following this basis, we can establish that octahedron is a polyhedral surface resulting from the polygonal system composed by eight triangles \( \Pi_1, \Pi_2, \Pi_3, \ldots, \Pi_n (n = 8) \) as it is illustrated in figure 1a. In the figure, the equivalent sides are denoted with a similar letter, and the polygonal vertexes match in a polyhedral vertex when the equivalent sides are identified. We can then follow the corresponding schematic combinatorial rule for this polygonal system, which is as:

\[
\Pi_1 : a, b, c; \quad \Pi_2 : a, d, e; \\
\Pi_3 : c, f, g; \quad \Pi_4 : g, h, i; \\
\Pi_5 : l, j, k; \quad \Pi_6 : k, l, b; \\
\Pi_7 : d, h, l; \quad \Pi_8 : c, f, j;
\]

Producing the polyhedral surface (Fig. 1b) and the corresponding representation in the Euclidian space (Fig. 1c) that are simply associated to the simplest aggregation form that the metals show.

For the decahedral polygonal system the known structure is defined by 10 triangles as it is illustrated in Fig. 2a, where...
by 20 triangles determined as $K_5$ polygons show no single orientation of its edges (Fig. 2c), which is associated to the configuration of the metal clusters, which is shown in Fig. 3b, while the Euclidian space view is also associated to the configuration of the metal clusters, which involves a two decahedrons structure with anti-symmetric array.

When the octahedron is truncated to produce six squares and eight triangles, it is formed the cubo-octahedron polygonal system with $C_i$ ($i = 1$ to 6) and $T_j$ ($j=1$ to 8), which is shown in figure 4a. It fulfills the following the combinatorial scheme

$$
T_1 : c, e, f; \quad C_1 : a^{-1}, d^{-1}, e^{-1}, b^{-1};
$$

$$
T_2 : d, n, m; \quad C_2 : a^{-1}, d^{-1}, h^{-1}, g^{-1};
$$

$$
T_3 : j, k, i; \quad C_3 : m^{-1}, l^{-1}, j^{-1}, e^{-1};
$$

$$
T_4 : a, p, l; \quad C_4 : p^{-1}, r^{-1}, q^{-1}, k^{-1};
$$

$$
T_5 : q, u, h; \quad C_5 : t^{-1}, w^{-1}, v^{-1}, u^{-1};
$$

$$
T_6 : g, v, b; \quad C_6 : x^{-1}, s^{-1}, o^{-1}, n^{-1};
$$

$$
T_7 : r, s, t; \quad C_7 : x, a, w.
$$

Producing consequently a surface as shown in figure 4b and a three-dimensional representation illustrated in Fig. 4c. The own morphology of this structure involves the representation of cubic system into a sphere.

Besides, when the truncation is such that triangles become hexagons with similar sides, the configuration is called tetraikadecahedron. The corresponding polygonal system is shown in figure 5a, with the hexagonal polygons ($H_m, C_n$ with $m=1$ to 8 and $n=1$ to 6). The corresponding combinatorial scheme that this polygonal systems is as:

$K_1 : 1, 2, 3; \quad K_2 : 1, 4, 5; \quad K_3 : 5, 6, 7;
$$

$K_4 : 7, 8, 9; \quad K_5 : 9, 10, 11; \quad K_6 : 11, 12, 13;
$$

$K_7 : 13, 14, 15; \quad K_8 : 15, 16, 17; \quad K_9 : 17, 18, 19;
$$

$K_{10} : 19, 20, 21; \quad K_{11} : 22, 23, 24; \quad K_{12} : 24, 25, 10;
$$

$K_{13} : 26, 27, 5; \quad K_{17} : 27, 6, 28; \quad K_{18} : 28, 29, 10;
$$

$K_{19} : 29, 14, 30; \quad K_{20} : 18, 26, 30; \quad K_{21} : 31, 32, 33;
$$

$K_{22} : 34, 35, 36; \quad K_{23} : 37, 38, 39; \quad K_{24} : 40, 41, 42;
$$

$K_{25} : 43, 44, 45; \quad K_{26} : 46, 47, 48; \quad K_{27} : 49, 50, 51;
$$

$K_{28} : 52, 53, 54; \quad K_{29} : 55, 56, 57; \quad K_{30} : 58, 59, 60; \quad K_{31} : 61, 62, 63; \quad K_{32} : 64, 65, 66.
$$

Producing consequently a surface as shown in figure 4b and a three-dimensional representation illustrated in Fig. 4c. The own morphology of this structure involves the representation of cubic system into a sphere.

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H_1:1, 2, 3, 4, 5, 6;
H_2:2', 11', 10', 9', 8', 7';
H_3:8, 12, 13, 14, 15, 16;
H_4:13', 21', 20', 19', 18', 17';
H_5:18, 22, 23, 24, 25, 26;
H_6:23', 28', 27', 26', 25', 24';
H_7:4', 33', 15', 32', 25', 31';
H_8:34, 10, 35, 29, 36, 20;
C_1:11, 1, 28, 35;
C_2:7, 16', 33, 3;
C_3:21, 12', 9, 34';
C_4:17', 26', 32, 14';
C_5:19, 36', 30, 22';
C_6:27, 5', 31, 24'.

Following this scheme, the corresponding induced surface is observed in Fig. 5b. With the Euclidian space view in Fig. 5c. The rounded profile has been experimentally distinguished and associated to the stability that it has. Similarly to the decahedron this system shows no single edges orientation for the square faces.

The Ino’s decahedron is considered of this lowest energy configurations family; identified as a truncated decahedron with a polygonal system formed by five rectangular and ten triangular faces (C_l and T_k with l = 1 to 5 and k = 1 to 10 respectively) generating a combinatorial scheme as following:

T_1 : 1, 2, 3;
T_2 : 2, 5', 4';
T_3 : 5, 6, 7;
T_4 : 6, 9', 8';
T_5 : 9, 1', 10;
T_6 : 10', 3', 13';
C_1 : 13, 4, 14, 15;
C_2 : 14', 7', 17', 16';
C_3 : 17, 8, 18, 19;
C_4 : 18', 10', 11, 20';
T_7 : 21', 15', 22';
T_8 : 23, 16, 24;
T_9 : 24', 19', 25';
T_{10} : 25', 20, 22'.

An identified surface as shown in figure 6b and the observation of the representation of this polygonal system in the Euclidian space in figure 6c. The rectangular faces become quite interesting, because this flat planes allow the production of one dimensional structures as the known as rods or wires [2,7].

Here, there is the topological research problem to identify when two different polygonal systems determine the same surface, it means, when the polyhedral surfaces resulting from the identification of equivalent points of two polygonal systems constitute different polygonal decomposition for the same surface. In fact, two polygonal systems focus to the same surface when they can be applied topologically one over the other, so equivalent points from the first one are transformed into equivalent points of the second one. This is not always possible (by instance when the surface does not have a particular orientation as the mentioned Klein bottle). For the considered structures, both have well defined orientation and consequently correspond to a similar classification.

The Euler feature of a surface polyedral is the number N = α_0 + α_1 − α_2. The analysis of this condition for the different metal clusters geometries considered here can be resumed in Table I. So the understanding of the smallest nanoparticle for each shape can be also sustained as following: α_0 is the amount of external atoms (vertex); α_1 is the number of linear
bonds that join those atoms; and \( \alpha_2 \) corresponds to the quantity of faces that compose the cluster. So the evaluation can be simply based on an analysis of the corresponding Euclidian views of Figs. 1-6. It is determined that in all the studied cases a similar Euler characteristic is fulfilled.

Because of these last considerations, the polygonal systems as cubo-octahedron and icosahedron and all the studied structures could be considered no topologically different. Particularly in case of the two signaled, for the resulting surface the important fact is the way that the extreme points \( p \) and \( q \) from the contour of a polygonal side are applied over the extreme points \( p' \) and \( q' \) of the correspondent side \( q' \) and no directly from the topological application of the side \( q' \) over the other side \( p' \). Consequently, there are just two essentially different applications for two different sides of a polygon. One of them identifies \( p \) with \( p' \) and the second involves \( q \) and \( q' \). By instance, of all the polygons are represented as rectilinear from the numerical plane, we can admit that the corresponding sides are applied between them by means of a linear application. This can be associated to the property of these kinds of clusters to transform one into the other [22]. Particularly Aragon has demonstrated in an elegant work that this atomistic array transformation can be studied as a linear transformation, using simple operators [10].

The study of the most representative geometries, which have been theoretically and experimentally determined, for small clusters allows identifying the powerful capabilities of these approaches and illustrates well the way that these must be studied and researched.

5. Conclusions

The structural models studied here are demonstrate to be topological similar and the possible mathematical operations can be applied indistinctly for them. Also the structures were plenty defined with help of the combinatorial schemes, making possible to interpret the kind of geometries that these clusters can adopt.

The evaluation of the topological systems and consequently the polyhedral surfaces allowed concluding also that:
- They are orientation capable and consequently they can show elemental transformations.
- It can be studied the relation and trajectories for their transformation and growing processes in basis of these topological principles.

The Euler condition establish a good parameter for understand the mechanisms that the nature follows in the selection of geometries at short scale as in the nanoparticles.

The use of topological approaches for the understanding of small metallic clusters open perspectives to study structural transformations, families and groups of configurations with similar properties. But it also gives the conditions about a formal method to explain and interpret the geometric conditions that induce the most stable systems. Consequently this work will be followed by deeper studies for particular structural processes and for a plenty understanding of geometrical systems as the ones that are found as metal clusters.

