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Technology
Multi-scale simulations of gold nanoparticles



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Abstract

Gold is a well-known precious metal that has been used in jewelry and coins since ancient times. Being the noblest of all metals, it is resistant to oxidation and corrosion. Gold nanoparticles show several interesting properties, such as changing color depending their size and shape and good activity as chemical reaction catalysts. Both their size and shape have key role in the efficiency of Au as catalysts.

The present master thesis presents a theoretical study of the relationship between structure and properties for gold nanoparticles. Using several different interatomic potentials and a continuum model, we calculate the surface energies of (111), (100) and (110) surfaces in good agreement to other theoretical calculations found in the literature.

We then construct models of nanoparticles of high symmetry and more specifically cubic, octahedral and rhombic dodecahedral nanoparticles in several sizes. The purpose of this study is to understand the role of the nanoparticle' s geometry on its properties and calculate the energies that determine the shape of these nanoparticles and provide for the first time calculations for edge and vertex energies of gold nanoparticles performed using a new atomistic model we developed.

Περίληψη

Ο χρυσός είναι ένα πολύ γνωστό πολύτιμο μέταλλο που χρησιμοποιούνταν σε κοσμήματα και νομίσματα κατά την αρχαιότητα. Όντας το πιο αδρανές από όλα τα μέταλλα, αντιστέκεται στην οξείδωση και την διάβρωση. Τα νανοσωματίδια χρυσού παρουσιάζουν αξιοσημείωτες ιδιότητες όπως η αλλαγή χρώματος ανάλογα το σχήμα και το μέγεθος τους και η δραστηκότητα τους ως καταλύτες χημικών αντιδράσεων. Το σχήμα και το μέγεθος των νανοσωματιδίων έχουν ρόλο κλειδί στην αποδοτικότητα τους ως καταλύτες.

Στην παρούσα μεταπτυχιακή διατριβή παρουσιάζουμε μια θεωρητική μελέτη της σχέσης δομής και ιδιοτήτων για νανοσωματίδια χρυσού. Χρησιμοποιώντας διαφορετικά δυναμικά και ένα συνεχές μοντέλο, υπολογίζουμε τις επιφανειακές ενέργειες των επιφανειών (111), (100) και (110) που είναι σε καλή συμφωνία με αποτελέσματα από άλλες θεωρητικές μελέτης που υπάρχουν στην βιβλιογραφία.

Στη συνέχεια κατασκευάζουμε νανοσωματίδια με υψηλή συμμετρία και πιο συγκεκριμένα κυβικά, οκταεδρικά και ρομβικά δωδεκαεδρικά σε διάφορα μεγέθη. Ο σκοπός της μελέτης είναι η κατανόηση του ρόλου που έχει η γεωμετρία του νανοσωματιδίου στις ιδιότητες τους και η παρουσίαση για πρώτη φορά υπολογισμών για τις ενέργειες των ακμών και των κορυφών που έγιναν με τη χρήση ενός νέου ατομιστικού μοντέλου που αναπτύξαμε.

2 Introduction

Gold is the chemical element with symbol Au, atomic number 79 and face center cubic (fcc) crystal structure (is shown in Figure 1). It is dense, soft, ductile and malleable metal with a pure yellow color. The word *gold* is cognate with similar words in other languages such as the Proto-Indo-European *ghel*, from which the word yellow came, while the symbol Au came from the latin word “aurum” which means bright dawn. It is a transition metal and belongs to the 11th group of the periodic table. Being the noblest of all metals, it is resistant to oxidation and corrosion. It is a precious metal that has been used in jewelry and coins since ancient times and it is a good conductor of heat and electricity. [1]

Gold nanoparticles present particular interest in nanotechnology. They are characterized by shape-related optoelectronic properties, large surface-to-volume ratio, excellent biocompatibility and low toxicity [2]. They also show interesting properties such as changing color depending on their shape and size and good activity as chemical reactions catalysts [2]. They can be used in many applications such as dental restoration (in the form of alloys) [3], therapeutics [4,5], detection and diagnostics [6], drug delivery systems [7], chemical and biological sensing [8], imaging [9], photovoltaics [10], probes for TEM [11]. Figure 2 shows gold nanoparticles in different shapes and sizes [12].

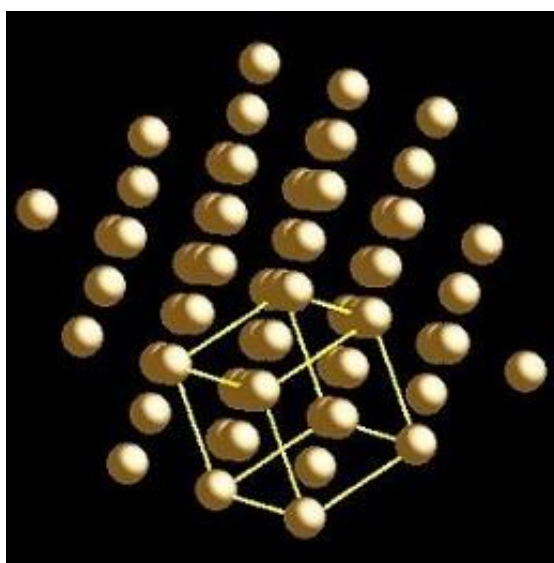


Figure 1: Gold crystal structure. Image is taken by webelements.com.

Gold is used as catalyst in many chemical reactions. In homogeneous catalysis, salts of Au(I) and Au(III) are used [13]. The activity of gold in combination with its resistance to air and moisture give it an advantage over other catalysts. Bulk metallic gold presents surface reactivity at room temperature only towards a few substances such as formic acid and sulphur-

containing-compounds (H_2S , thiols) [14]. In heterogeneous catalysis, the adsorption of reactants is improved by using gold nanoparticles on solid polymeric or inorganic substrates (CeO_2 , Fe_2O_3 , TiO_2) [15].

Two well-known types of catalytic reactions that employ gold nanoparticles are a) the oxidation by O_2 which include the oxidation of CO in mild temperatures, the alcohol oxidation the direct synthesis of hydrogen peroxide and alkene epoxidation and b) hydrogenation where gold nanoparticles supported on metal oxides such us SiO_2 , Al_2O_3 , ZnO etc. are used for selective hydrogenation of organic molecules i.e. α,β -unsaturated aldehydes, unsaturated ketones and unsaturated hydrocarbons. [16]

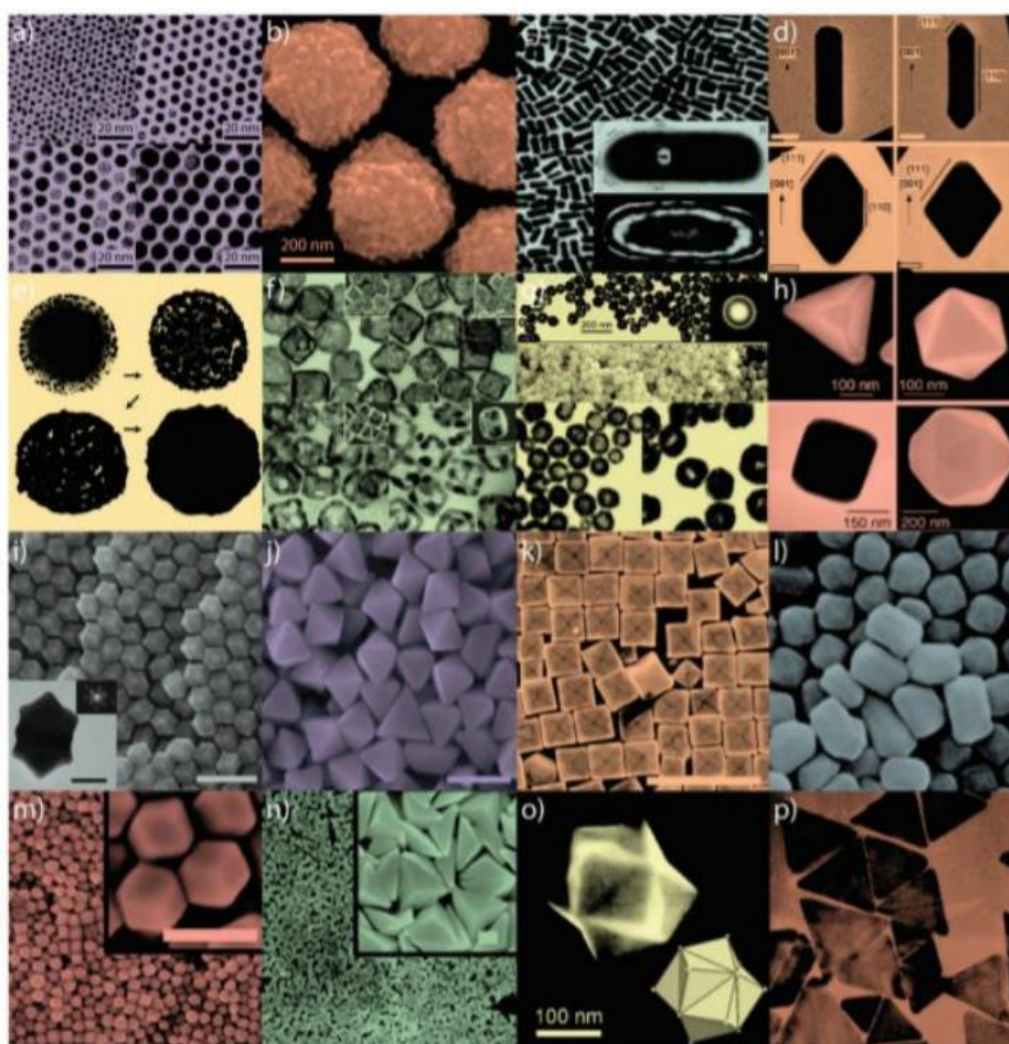


Figure 2: gold nanoparticles in several shapes and sizes. a) small and b) large nanospheres, c) nanorods, d) sharpened nanorods, e) nanoshells, f) nanocages, g) hollow nanospheres, h) tetrahedral/octahedra/cubes/icosahedra, i) rhombic dodecahedra, j) octahedral, k) concave nanocubes, l) tetrahexahedra, m) rhombic dodecahedra, n) obtuse triangular bipyramids, o) trisoctahedra and p) nanoprisms. [12]

The efficiency of gold nanoparticles depends on their size and shapes. It is known that the reactivity of gold nanoparticles is due to the low coordinated atoms [17]. In the case of CO oxidation, the adsorption of CO takes place at the edges and the corners while the activation of oxygen occurs at peripheral sites. It has been proven that nanoclusters with size 1-5 nm have amazing properties but larger nanoclusters are catalytically inactive. The size of the nanoparticles also affects quantum phenomena due to the spatial confinement of valence electrons [14].

The present master thesis presents a theoretical study for gold nanoparticles and surfaces. In chapter 2 we investigate the connection between structure and properties for gold nanoparticles. In chapter 3, using a continuous model and several interatomic potentials we calculate the surface energies of (111), (100) and (110) surfaces in good agreement to other theoretical calculations found in the literature. Finally, in chapter 4, we construct models of nanoparticles high symmetry and more specifically cubic, octahedral and rhombic dodecahedral nanoparticles. The main purpose of this study is to understand the way that the nanoparticle's shape connects to its properties. For the first time, we provide calculations for edge and vertex energies of gold nanoparticles performed using a new atomistic model we develop and several interatomic potentials.

3 Gold nanoparticles

Before we start talking about nanoparticles and their shapes, we need to explain what a nanoparticle is. A nanoparticle is a set of N atoms with an external polyhedral shape. A typical size of a nanoparticle ranges from 1 to 100 nm in at least one direction. This scale size differentiates their physical, chemical and biological properties in relation to the properties of atoms or molecules. Their consistent use is due to well-defined methods for their composition and handling.

The shape of the nanoparticles affects their functionality in applications such as photonics, plasmonics, sensing and biolabeling. The nanoparticles usually are found in their equilibrium shape which can be predicted by minimizing Gibbs energy:

$$G = G_{bulk} + \sum_{hkl} A_{hkl} \gamma_{hkl}$$

where G_{bulk} is the free energy of the bulk material, γ_{hkl} is the required energy to create a surface of unit area that is parallel to the (hkl) plane of the crystal and A_{hkl} is the surface. Under thermodynamic equilibrium and since G_{bulk} is constant, the Gibbs energy is minimized when the total surface energy $\sum_{hkl} A_{hkl} \gamma_{hkl}$ gets its minimum value. [18, 19]

At the beginning of the 20th century, G. Wulff found a simple way to predict the shape of the particles of crystal solids. Theoretical simulations based on Wulff construction has been developed and help us to predict the shape of the nanoparticles without using difficult mathematical expressions. Wulffman and VESTA are free for Wulff construction are two examples of free software that can be used to visualize for Wulff construction. [18-21]

Several decades after Gibbs, George Wulff proposed his theory. According to what is now called the Wulff theorem, the shape that minimizes the total surface energy from Gibbs formula is the shape which the distance of (hkl) face from the center of the nanoparticle is proportional to its surface energy. Therefore, the distance of any (hkl) face can be calculated as:

$$d_{hkl} = d_{h'k'l'} \frac{\gamma_{hkl}}{\gamma_{h'k'l'}} \quad (1)$$

where γ_{hkl} and $\gamma_{h'k'l'}$ are the surface energies of (hkl) and $(h'k'l')$ faces respectively and $d_{h'k'l'}$ is the distance of $(h'k'l')$ plane from the center and determines the size of the nanoparticle.

The resulting equilibrium shape is a closed polyhedron with the following properties:

- i. The shape doesn't depend on the absolute values of surface energies but it depends on their ratios.
- ii. High-index (hkl) surfaces usually have higher surface energy than low-index surfaces.
- iii. High-index (hkl) surfaces are steeper and usually are hidden behind low-index surfaces and they tend to occupy smaller areas in the equilibrium shape even if γ_{hkl} is low.
- iv. The extra energy required to form edges and vertices are not taken into account.
- v. The polyhedral belongs to the same point group as the crystal structure of the material.

In order to find the equilibrium shape of the nanoparticle, we choose one plane i.e (111) and we draw it up at a distance d_{111} . Then, we draw up any plane (hkl) at a distance $d_{hkl} = d_{111} \frac{\gamma_{hkl}}{\gamma_{111}}$. [18-21]

The purpose of this chapter is to understand how the structure affects the properties of the nanoparticle. We construct models of nanoparticles with high symmetry and more specifically cubic, octahedral and rhombic dodecahedral nanoparticles and we calculate the number of the nearest neighbors of each atom (coordination number). We then find formulas for the number of atoms with the same coordination number as a function of the total number of atoms of the nanoparticle. We also explain the relationship between the coordination number of an atom with its position.

We used a home-made code for constructing nanoparticles for simulations, which uses extensively the Atomic Simulation Environment (ASE) library. Using this code, we constructed cubic, octahedral and rhombic dodecahedral nanoparticles. In these high-symmetry shapes, all faces of each nanoparticle have identical crystalline orientation: (100) for cube, (111) for octahedron and (110) for rhombic dodecahedron.

Several sizes of the nanoparticles were constructed using ASE; cubic nanoparticles ranged from 63 to 1342810 atoms, octahedral nanoparticles ranged from 85 to 646899 atoms and rhombic dodecahedral nanoparticles ranged from 93 to 447717 atoms. All nanoparticles have no imperfections and all the atoms are located in their ideal fcc positions. We calculated coordination numbers of gold atoms (number of nearest –neighbors of each atom) using a Python code and then we calculated the number of atoms of each nanoparticle with the same coordination number. Atoms with different coordination number were represented using different colors when visualizing.

3.1 Active sites

Atoms in each nanoparticle have different contributions depending on their type. For example, for each catalytic reaction only few atoms of the nanoparticle serve as binding sites for the reactants and the products. These are called active sites. The turnover frequency (TOF) of a catalyst, which is mass of reaction products per unit time per unit time per catalyst mass, is proportional to the active site density, n . In most cases, active sites of a nanoparticle are atoms at the facets, the edges or the vertices. The active sites density express the μmol of the active sites of catalyst per g of catalyst and it can be calculated as following

$$n = \frac{N_i * 10^6}{N * A}$$

where N_i is the number of active sites, N is the total number of sites or the total number of atoms and $A = 196.67 g/mol$.

We calculate the active sites density of all the sizes and shapes of nanoparticles and the results are shown in Tables 1 to 9 of the next section. We notice that as we increase the number of atoms of a nanoparticle, regardless the shape, active sites density decreases for all possible active sites. For example, the atoms at the edges of a cubic nanoparticle have 5 nearest neighbors. As atoms are added to the nanoparticle, the number of atoms with 5 neighbors increases. On the other hand, the number of bulk atoms increases too, but at a higher rate. As a result, the percentage of atoms with 5 nearest neighbors decreases and thus active sites also decreases.

We conclude that increase in the size of the nanoparticle leads to decrease in active sites density and consequently to a reduction in the TOF. As a result, large nanoparticle are not effective catalysts.

3.2 Cubic Nanoparticles

Cube is the polyhedral with 6 square facets of the (100) type, 12 edges and 8 vertices. Let l be the edge length, A be the total nanoparticle's surface and V the total volume. Then:

$$V = l^3, A = 6l^2.$$

Tables 1 and 2 and 3 present the numbers of atoms with the same coordination number for three different cubic nanoparticles with 365, 7813 and 45563 atoms respectively. Figure 3 show a typical cubic nanoparticle with size of 7813 atoms.

We observe that atoms in the bulk have 12 neighbors, the atoms of the facets have 8 neighbors, the atoms of the edges have 5 neighbors and the atoms of the vertices have 3 neighbors.

From Tables 1 and 2 and Figure 3 we can clearly see that only the 8 atoms of the vertices have 3 neighbors so

$$N_3 = 8 ,$$

where N_3 is the number of atoms with 3 nearest neighbors, regardless the total number of atoms of the nanoparticle. Smaller nanoparticles (≤ 365 atoms) have fewer atoms with 12 neighbors (bulk) while there are more atoms with 5 and 8 in total. However, as the size of the nanoparticle increases, the number of bulk atoms ($z = 12$) dramatically increases while the number of atoms on the facets ($z = 8$) or edges ($z = 5$) increases but not at the same rate. On the other hand, if we observe the corresponding percentages we will see that only the percentage of atoms with $z = 12$ increases while the other percentages decrease. As the nanoparticle size increases, both its total surface and volume increase, but the surface to volume ratio decreases.

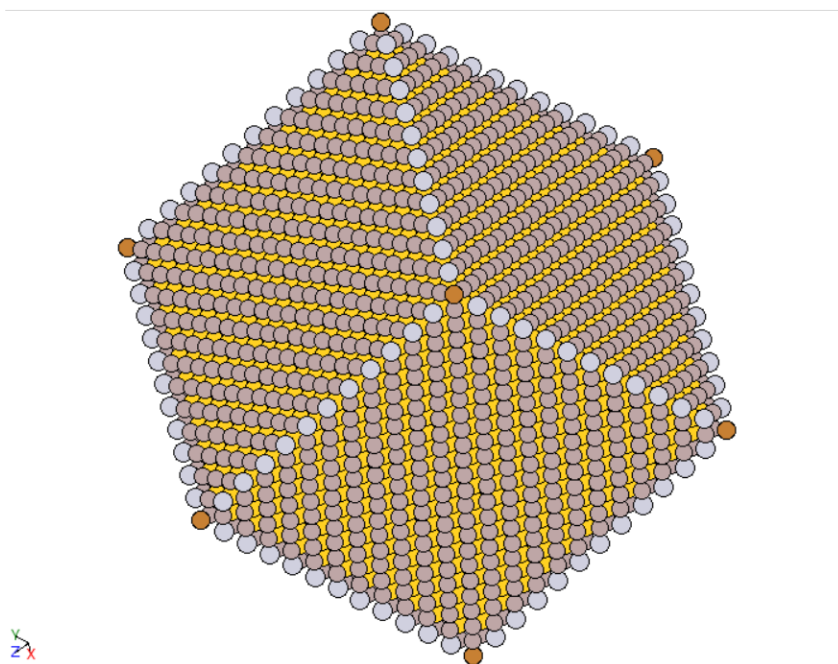


Figure 3: A typical cubic nanoparticle with 7813 atoms. Different colors represent atoms with different coordination number; copper atoms have $z = 3$, silver atoms have $z = 5$, gray atoms have $z = 8$ and yellows have $z = 12$ where z is the coordination number.

Table 1: Types of atoms in a cubic nanoparticle with 365 atoms with different coordination numbers (z). N_z is the number of atoms with z neighbors, N_{tot} is the total number of atoms and n_z is the active-site density (in $\mu\text{mol/g}$) for atoms with z neighbors.

z	N_z	N_z/N_{tot}	n_z
3	8	2.19	111.3
5	36	9.86	501.
8	150	41.1	2090.
12	171	46.8	2379
N_{tot}	365		

Table 2: Same as Table 1 for cubic nanoparticle with 7813.

z	N_z	N_z/N_{tot}	n_z
3	8	0.10	5.2
5	132	1.69	85.8
8	1590	20.4	1033.
12	6083	77.9	3953
N_{tot}	7813		

Table 3: Same as Table 1 for cubic nanoparticle with 45563.

z	N_z	N_z/N_{tot}	n_z
3	8	0.02	0.89
5	252	0.55	28.1
8	5550	12.2	519.
12	39753	87.2	4430
N_{tot}	45563		

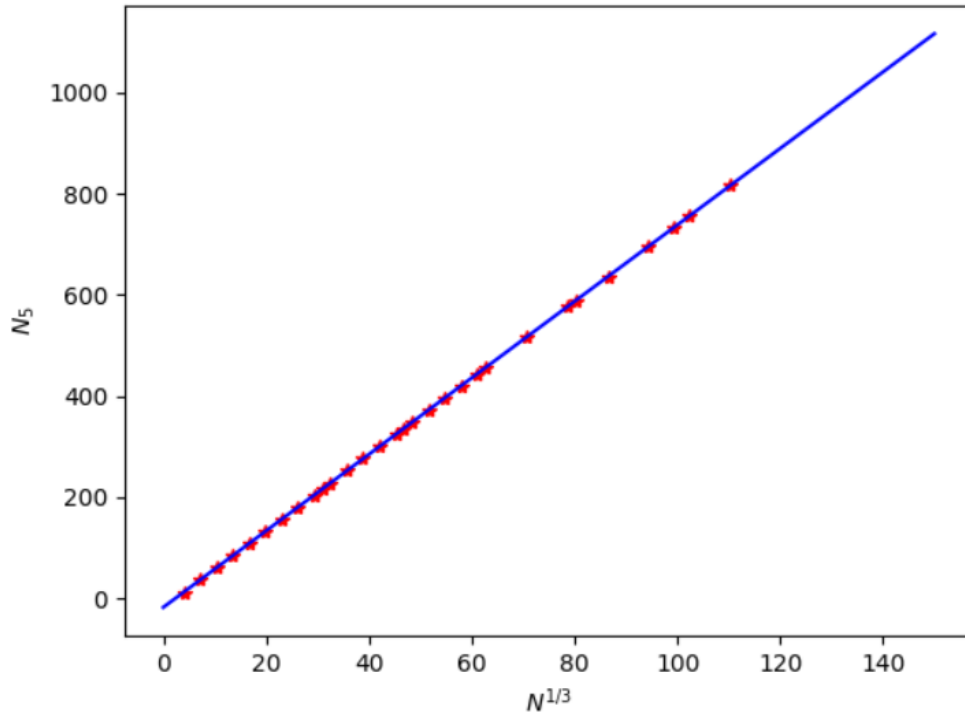


Figure 4: Figure 4: The number of atoms with $z = 5$ as a function of $N^{1/3}$ for cubic nanoparticles.

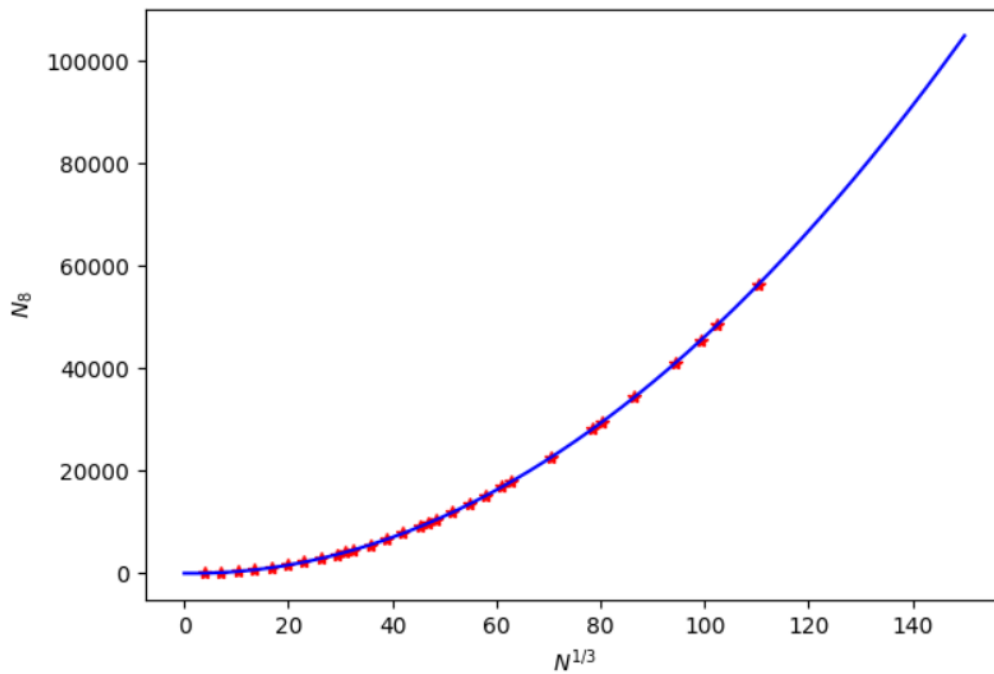


Figure 5: Same as Figure 4 for $z = 8$ for cubic nanoparticles.

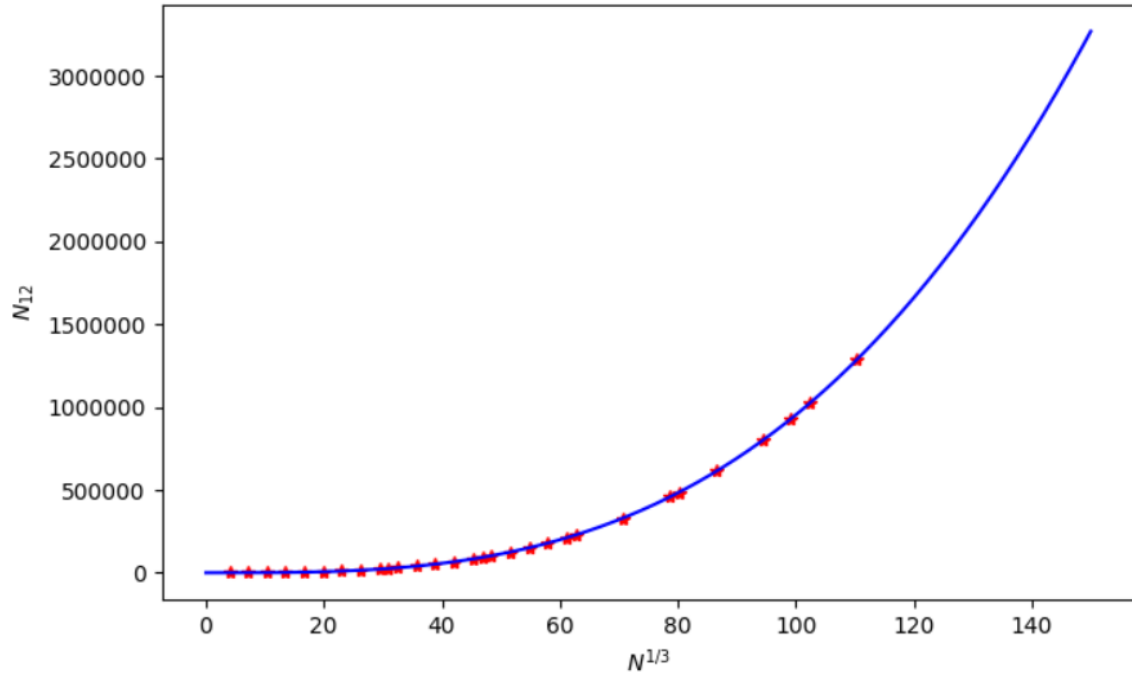


Figure 6: Same as Figure 4 for $z = 12$ for cubic nanoparticles.

In the following, we will use these data to find mathematical formulas for the number of atoms with given number of nearest neighbors as a function of the total number of atoms. As mentioned before,

$$N_3 = 8$$

regardless the size of the nanoparticle. If we consider that D is the diameter of the gold atom then each edge of the cubic nanoparticle has $\frac{l}{D} - 2$ atoms because every edge is connected with 2 edges. So the total number of atoms with coordination number $z = 5$ is

$$N_5 = 12\left(\frac{l}{D} - 2\right).$$

It is known that $V = NV_{at}$ where V_{at} is volume per atom and N is the total number of atoms, therefore

$$N_5 = 12\left(\frac{V_{at}^{\frac{1}{3}}}{D} N^{\frac{1}{3}} - 2\right) \quad (2).$$

Due to the difficulty in measuring the number of atoms at the facets we will use Table 2 and Figure 3 as an aid. The main idea here is to find how many atoms one face of the cube has and then try to convert this number as a function of $\frac{l}{D}$. Let's take as example the nanoparticle with 7813 atoms. In Figure 3 we count

the number of atoms which are on an edge and add the 2 atoms of the vertices and we find that $\frac{l}{D}=13$. This nanoparticle has 1590 atoms at the faces so each face has 265 atoms. But 265 is written as $265 = 2 * 11 * 12 + 1$ which means that each face has $2\left(\frac{l}{D} - 2\right)\left(\frac{l}{D} - 1\right) + 1$ atoms, so

$$N_8 = 6 \left[2 \left(\frac{l}{D} - 2 \right) \left(\frac{l}{D} - 1 \right) + 1 \right] \Rightarrow$$

$$N_8 = 12 \frac{V_{at}^{\frac{2}{3}}}{D^2} N^{\frac{2}{3}} - 36 \frac{V_{at}^{\frac{1}{3}}}{D} N^{\frac{1}{3}} + 30 \quad (3).$$

Finally, we know that

$$N_{12} = N - N_3 - N_5 - N_8.$$

Therefore,

$$N_{12} = N - 12 \frac{V_{at}^{\frac{2}{3}}}{D^2} N^{\frac{2}{3}} + 24 \frac{V_{at}^{\frac{1}{3}}}{D} N^{\frac{1}{3}} - 36 \quad (4).$$

Figures 4, 5 and 6 represents the fittings of the number of neighbors with a specific coordination number (5, 8 or 12) as a function of $N^{1/3}$. The red stars symbolize our data while the blue line is the curve fitting by Python. The mathematical formulas (2),(3) and (4) are in agreement with the thermodynamic limit $L \sim N^{1/3}$, $A \sim N^{2/3}$ and $V \sim N$. In all cases, the proposed equations present excellent fitting of the results.

3.3 Octahedral nanoparticles

The next shape we will focus on is octahedron. Octahedron consists of 8 facets of (111) type, 12 edges and 6 vertices. Defining l to be the edge length, the total surface A and the volume V can be expressed as:

$$A = 2\sqrt{3}l^2, \quad V = \frac{\sqrt{2}}{3}l^3$$

Tables 4, 5 and 6 show the results for the coordination number of three octahedral nanoparticles consisting of 231, 8119 and 45961 atoms and Figure 7 presents a model of a nanoparticle of 8119 atoms. We observe that the atoms at the vertices have 6 neighbors, the atoms at the edges have 7 neighbors, the atoms at the facets have 9 neighbors and the bulk atoms have 12 neighbors as in the cube.

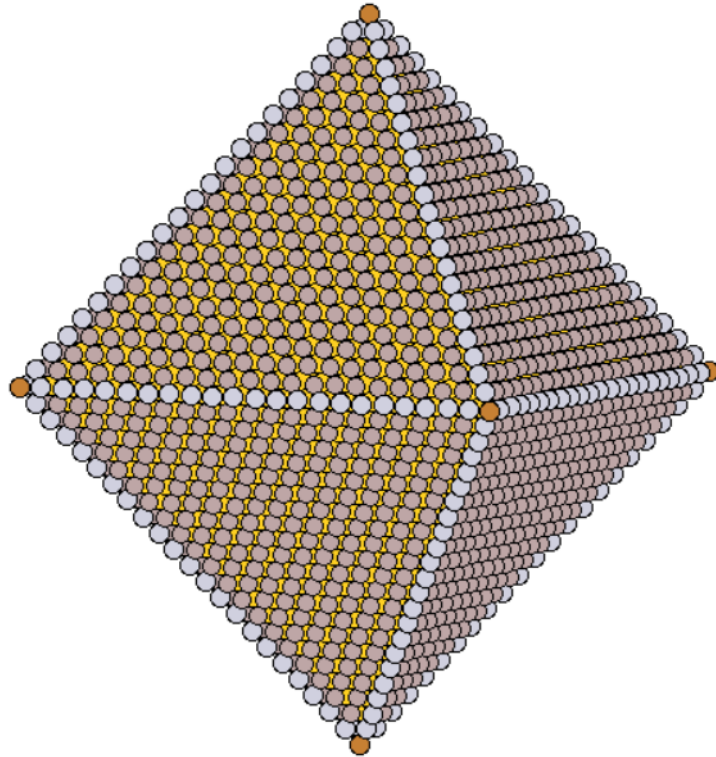


Figure 7: A typical octahedral nanoparticle with 8119 atoms. Different colors represent atoms with different coordination number; atoms have $z = 4$, silver atoms have $z = 7$, gray atoms have $z = 9$ and yellows have $z = 12$ where z is the coordination number.

Table 4: Same as Table 1 for octahedral nanoparticle with 231 atoms.

z	N_z	N_z/N_{tot}	n_z
4	6	2.6	132
7	60	26	1320
9	80	34.6	1760
12	85	36.8	1870
N_{tot}	231		

Table 5: Same as Table 1 for octahedral nanoparticle with 8119 atoms.

z	N_z	N_z/N_{tot}	n_z
4	6	0.07	3.75
7	252	3.10	158
9	1680	20.7	1050
12	6181	76.1	3870
N_{tot}	8119		

Table 6: Same as Table 1 for octahedral nanoparticle with 45961 atoms.

z	N_z	N_z/N_{tot}	n_z
4	6	0.013	0.66
7	468	1.02	51.7
9	5928	12.8	655
12	39559	86.1	4370
N_{tot}	45961		

Octahedral nanoparticles show similarities with cubic ones. Of course, bulk atoms have the same coordination number ($z = 12$). Atoms of the edges and facets don't have the same coordination number with the atoms at the corresponding positions in cubic nanoparticles. As the size of the nanoparticle gets bigger the atoms at the edges and the facets increase but not too fast as bulk atoms. Also, the number of atoms with the lower coordination number is constant and these atoms are at the vertices of the nanoparticle.

Now we find formulas for the number of atoms with specific number of neighbors as a function of the total number of atoms. As it mentioned above, atoms with 4 neighbors are located at the vertices and the number of them remains constant, therefore

$$N_4 = 6.$$

Each edge of the nanoparticle has $\frac{l}{D} - 2$ atoms because every edge is connected to 2 edges. Then, the total number of atoms which have 7 neighbors can be expressed by the formula:

$$N_7 = 12\left(\frac{l}{D} - 2\right).$$

Using the relationships $V = NV_{at}$ and $V = \frac{\sqrt{2}}{3}L^3$, we end up in the formula:

$$N_7 = 12 \left(\frac{\left(\frac{3}{\sqrt{2}}V_{at}\right)^{\frac{1}{3}}}{D} N^{\frac{1}{3}} - 2 \right) \quad (5).$$

We will count the number of atoms at the facets using the same procedure we followed for cubic nanoparticles. We will use as an example the octahedral nanoparticle with 8119 atoms which is shown in Figure 7 and we find that $\frac{l}{D} = 23$. From Table 5 we know that this nanoparticle has 1680 atoms at the facets so each face has 210 atoms. Number 210 is written as $210 = \frac{1}{2} * 21 * 20$ which

means that each face has $\frac{1}{2}\left(\frac{l}{D}-2\right)\left(\frac{l}{D}-3\right)$ atoms so the total number of atoms with coordination number $z = 9$ is given:

$$N_9 = 8 \left[\frac{1}{2} \left(\frac{l}{D} - 2 \right) \left(\frac{l}{D} - 3 \right) \right] = 4 \left(\frac{l}{D} - 2 \right) \left(\frac{l}{D} - 3 \right) \Rightarrow$$

$$N_9 = 4 \left(\frac{\left(\frac{3}{\sqrt{2}} V_{at} \right)^{\frac{1}{3}}}{D} \right)^2 N^{\frac{2}{3}} - 20 \left(\frac{\left(\frac{3}{\sqrt{2}} V_{at} \right)^{\frac{1}{3}}}{D} \right) N^{\frac{1}{3}} + 24 \quad (6).$$

The number of the bulk atoms can be easily calculated:

$$N_{12} = N - N_4 - N_7 - N_9 \Rightarrow$$

$$N_{12} = N - 4 \left(\frac{\left(\frac{3}{\sqrt{2}} V_{at} \right)^{\frac{1}{3}}}{D} \right)^2 N^{\frac{2}{3}} + 8 \left(\frac{\left(\frac{3}{\sqrt{2}} V_{at} \right)^{\frac{1}{3}}}{D} \right) N^{\frac{1}{3}} - 6 \quad (7).$$

Equations (5), (6) and (7) are analogous to equations (2), (3) and (4) as we expected. In Figures 8, 9 and 10 we see the fittings of the number of neighbors with the same coordination number (7, 9 or 12) as a function of $N^{1/3}$. The red stars symbolize our data while the blue line is the curve fitting by Python.

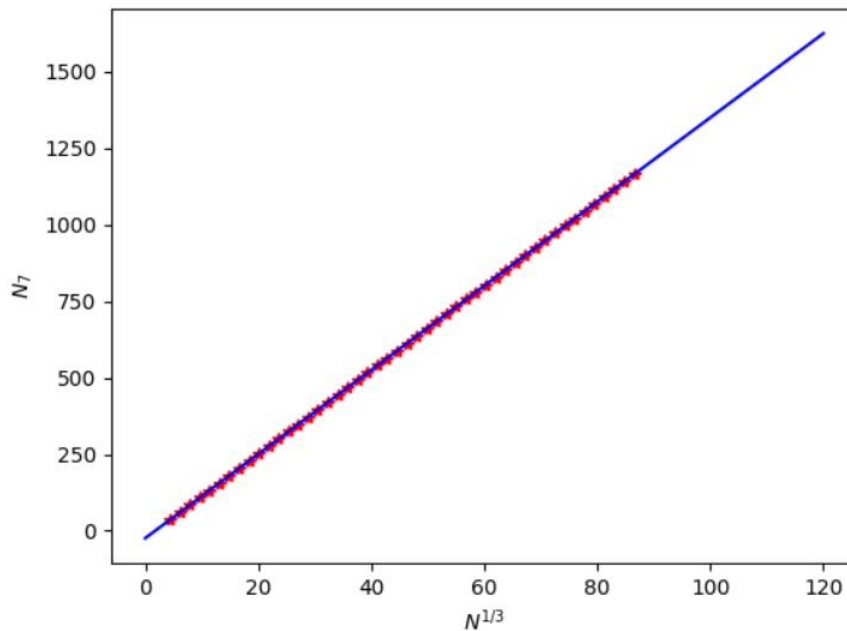


Figure 8: Same as Figure 4 for $z = 7$ for octahedral nanoparticles.

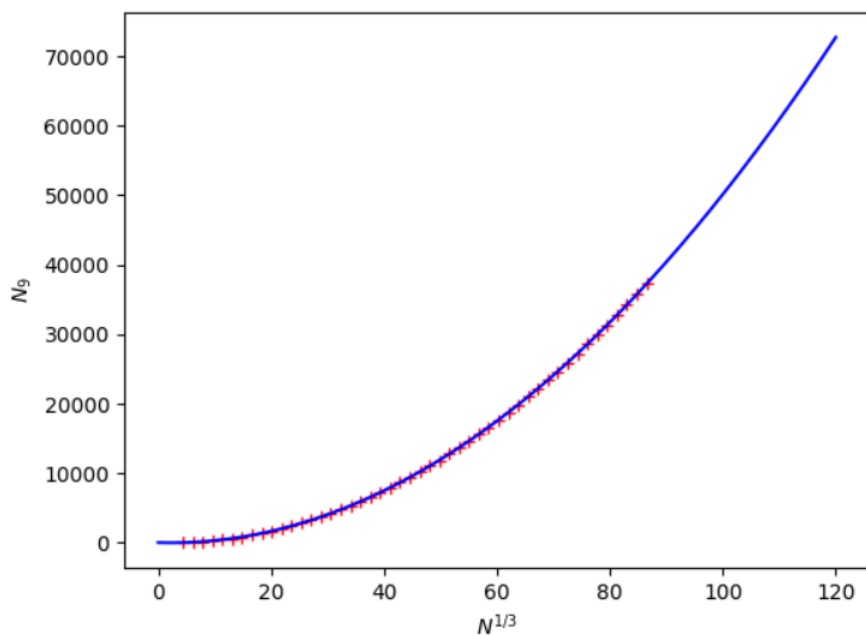


Figure 9: Same as Figure 4 for $z = 9$ for octahedral nanoparticles.

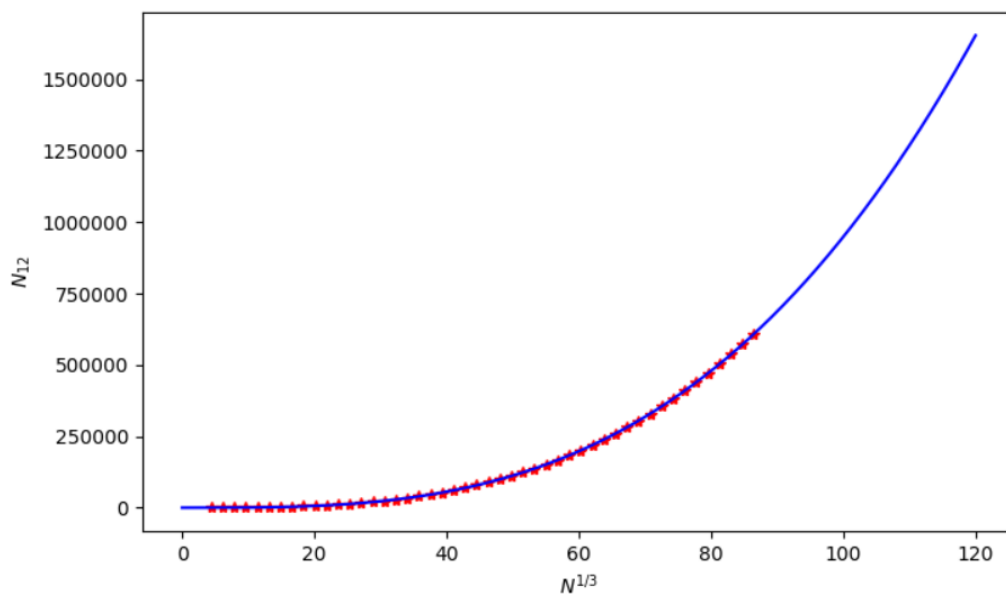


Figure 10: Same as Figure 4 for $z = 12$ for octahedral nanoparticles.

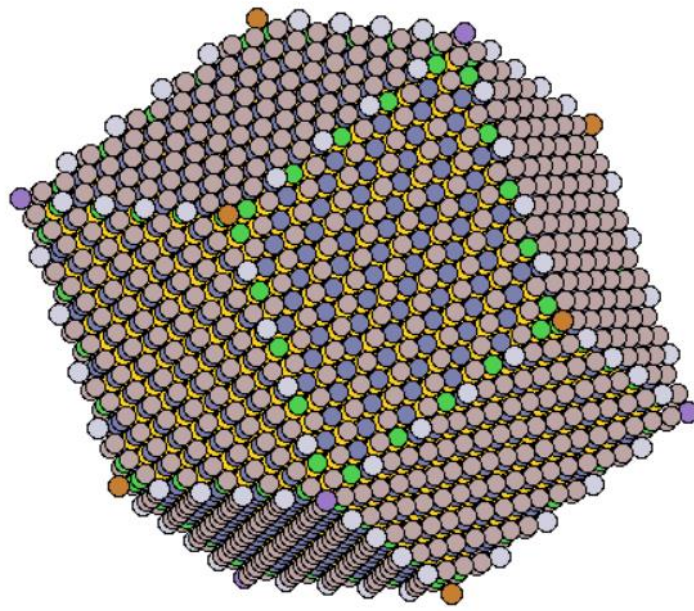


Figure 11: A typical rhombic dodecahedral nanoparticle with 8621 atoms. Different colors represent atoms with different coordination number; copper and purple atoms have $z = 3$ and $z = 4$, silver and green atoms have $z = 5$ and $z = 10$, gray and blue atoms have $z = 7$ and $z = 11$ and yellow atoms have $z = 12$.

3.4 Rhombic dodecahedral nanoparticles

The final shape is rhombic dodecahedron that has 12 rhombic facets of (110) type, 24 edges and 14 vertices of two types. The total area and volume of the rhombic dodecahedron of edge length L are:

$$A = 8\sqrt{2}l^2, \quad V = \frac{16\sqrt{3}}{9}l^3.$$

Tables 7, 8 and 9 presents a list for coordination number of three different nanoparticles with 617, 8621 and 48637 atoms while Figure 11 shows a rhombic dodecahedral nanoparticle with 8621 atoms.

Rhombic dodecahedral nanoparticles differ from cubic and octahedral ones and their differentiation is due to their polymorphism in the coordination number of atoms. Initially, rhombic dodecahedron has two types of vertices, 8 vertices of one type and 6 of the other, so in these positions we can find atoms with 3 or 4 neighbors. Another difference is that there are two different types of atoms on the faces. If we look very carefully Figure 11 we will see that in the gaps between gray atoms ($z = 7$) there are blue atoms ($z = 11$) at a lower level.

Therefore, a lower surface level is created. A similar situation exists in edges where we have the so-called steps and the atoms have two possible coordination numbers. Silver atoms ($z = 5$) are higher than green atoms ($z = 10$).

Despite the complexity of these nanoparticles, the dependence of the number of atoms that have certain number of neighbors on their total number of atoms is similar to that of cubic and octahedral nanoparticles. As in the two other cases, when the increase the nanoparticle size, the bulk atoms increase at a much faster rate than those found on the facets, and those increase faster than those on the edges. The number of atoms at the vertices, as always, remains constant as the size increase, thus

$$N_3 = 8$$

and

$$N_4 = 6.$$

Table 7: Same as Table 1 for rhombic dodecahedral nanoparticle with 617 atoms.

z	N_z	N_z/N_{tot}	n_z
3	8	1.30	65.8
4	6	0.97	49.4
5	24	3.89	197
7	156	25.3	1280
10	48	7.78	395
11	96	15.6	790
12	279	45.2	2300
N_{tot}	617		

Table 8: Same as Table 1 for rhombic dodecahedral nanoparticle with 8621 atoms.

z	N_z	N_z/N_{tot}	n_z
3	8	0.093	4.71
4	6	0.07	3.53
5	96	1.11	56.5
7	1092	12.7	643.
10	120	1.39	70.7
11	960	11.1	565
12	6339	73.5	3730
N_{tot}	8621		

Table 9: Same as Table 1 for rhombic dodecahedral nanoparticle with 48637 atoms.

z	N_z	N_z/N_{tot}	n_z
3	8	0.016	0.84
4	6	0.012	0.63
5	192	0.38	20.
7	3684	7.56	385
10	216	0.44	22.5
11	3456	7.11	361
12	41075	84.4	4290
N_{tot}	48637		

Each edge has $\frac{l}{D} - 2$ atoms thus the total number of atoms at the edges is

$$N_e = 24\left(\frac{l}{D} - 2\right).$$

From Tables 7, 8 and 9 we notice that the number of atoms with $z = 10$ is equal to the number of atoms with $z = 5$ increased by 24. Thus,

$$N_5 + N_{10} = 24\left(\frac{l}{D} - 2\right)$$

and

$$N_{10} = N_5 + 24.$$

Based on the above, we end up in the relationships:

$$N_5 = 12\left(\frac{l}{D} - 3\right)$$

and

$$N_{10} = 12\left(\frac{l}{D} - 1\right).$$

Using the relationships $V = NV_{at}$ and $V = \frac{16}{9}\sqrt{3}L^3$, the final relationships are:

$$N_5 = 12 \frac{\left(\frac{9}{16\sqrt{3}}V_{at}\right)^{\frac{1}{3}}}{D} N^{\frac{1}{3}} - 36 \quad (8)$$

and

$$N_{10} = 12 \frac{\left(\frac{9}{16\sqrt{3}}V_{at}\right)^{1/3}}{D} N^{1/3} - 12 \quad (9).$$

It is more difficult to count the atoms with 7 or 11 neighbors which located at surfaces for rhombic dodecahedral nanoparticles. Here, we will use the nanoparticle with 8621 atoms. From Figure 11 we count that $\frac{l}{D} = 11$. From Table 8 we know we have 1092 atoms with $z = 7$ at the facets so each face has 91 atoms. But 91 is written as $91 = 10 * 9 + 1$. This means that each face has $\left(\frac{l}{D} - 1\right)\left(\frac{l}{D} - 2\right) + 1$ atoms with 7 neighbors. Thus

$$N_7 = 12 \left[\left(\frac{l}{D} - 2\right)\left(\frac{l}{D} - 1\right) + 1 \right] \Rightarrow$$

$$N_7 = 12 \frac{\left(\frac{9}{16\sqrt{3}}V_{at}\right)^{2/3}}{D^2} N^{2/3} - 36 \frac{\left(\frac{9}{16\sqrt{3}}V_{at}\right)^{1/3}}{D} N^{1/3} + 36 \quad (10).$$

On the other hand, the nanoparticle has 960 atoms at the facets with $z = 11$ so each face has 80 atoms which is written as $80 = 8 * 10$. Thus each face has $\left(\frac{l}{D} - 3\right)\left(\frac{l}{D} - 1\right)$ atoms. We conclude that the number of atoms with 11 neighbors are

$$N_{11} = 12 \left(\frac{l}{D} - 3\right)\left(\frac{l}{D} - 1\right) \Rightarrow$$

$$N_{11} = 12 \frac{\left(\frac{9}{16\sqrt{3}}V_{at}\right)^{2/3}}{D^2} N^{2/3} - 48 \frac{\left(\frac{9}{16\sqrt{3}}V_{at}\right)^{1/3}}{D} N^{1/3} + 36 \quad (11).$$

Finally, the number of bulk atoms is given by the formula

$$N_{12} = N - N_3 - N_4 - N_5 - N_7 - N_{10} - N_{11} \Rightarrow$$

$$N_{12} = N - 24 \frac{\left(\frac{9}{16\sqrt{3}}V_{at}\right)^{2/3}}{D^2} N^{2/3} + 60 \frac{\left(\frac{9}{16\sqrt{3}}V_{at}\right)^{1/3}}{D} N^{1/3} - 38 \quad (12).$$

Despite the fact that at the edges and the surfaces of a rhombic dodecahedral nanoparticle there are atoms with two different coordination number, the predictions we made in the previous cases are confirmed again. The number of atoms with $z = 5$ or $z = 10$ is a function of $N^{1/3}$ since being at the edges. On the other hand, the number of the atoms at the surfaces is a function of $N^{2/3}$ while the number of bulk atoms depends on N . These observations are confirmed by Figures 12, 13, 14, 15 and 16 which presents the fittings. The red stars symbolize our data while the blue line is the curve fitting by Python.

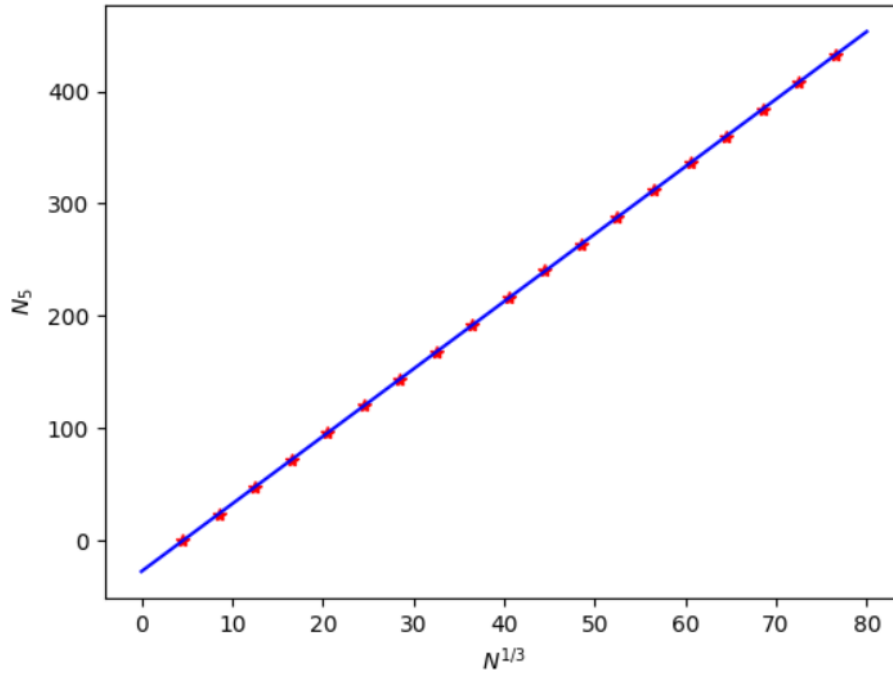


Figure 12: Same as Figure 4 for $z = 5$ for rhombic dodecahedral nanoparticles.

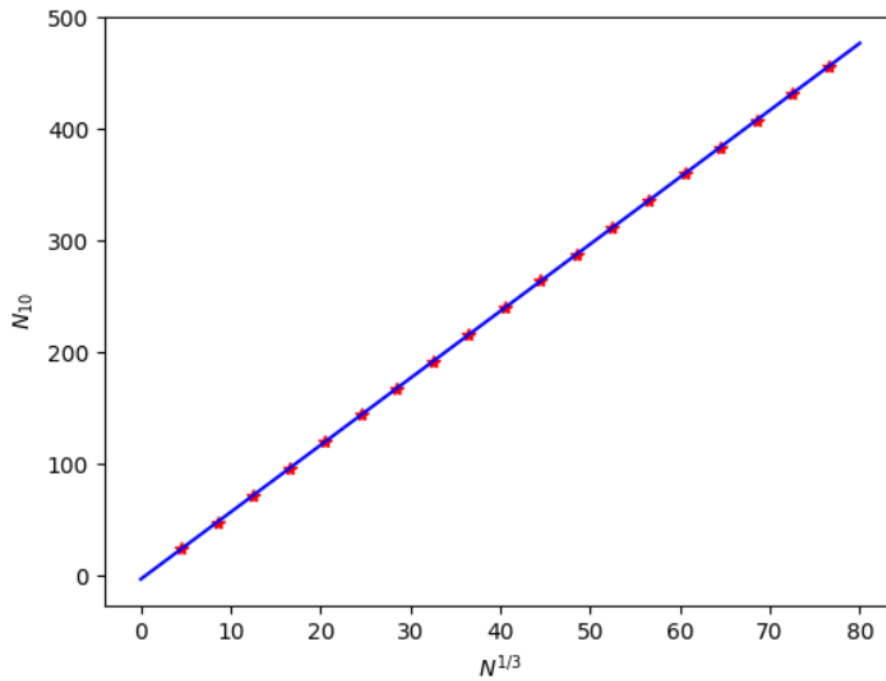


Figure 13: Same as Figure 4 for $z = 10$ for rhombic dodecahedral nanoparticles.

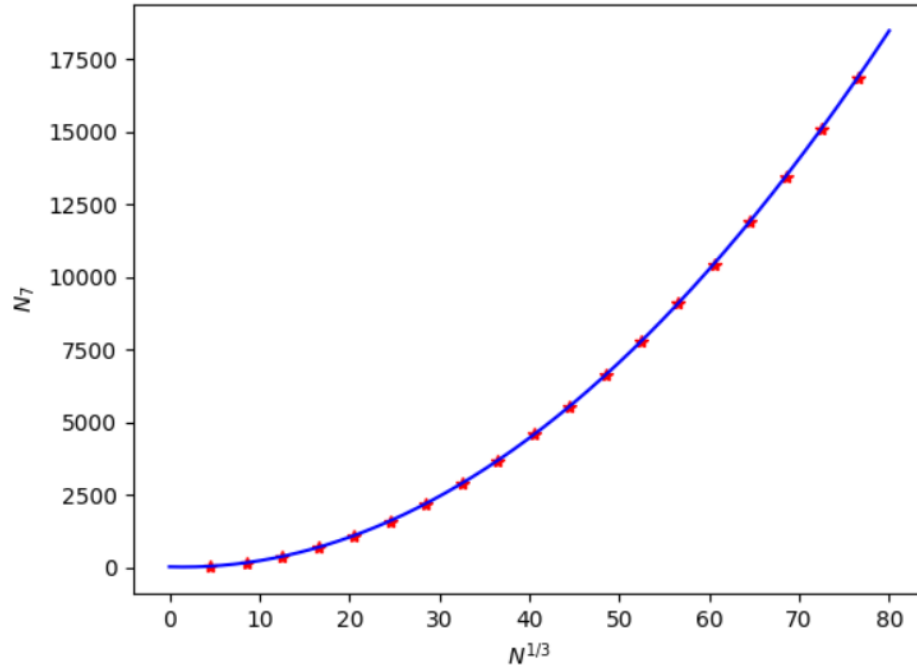


Figure 14: Same as Figure 4 for $z = 7$ for rhombic dodecahedral nanoparticles.

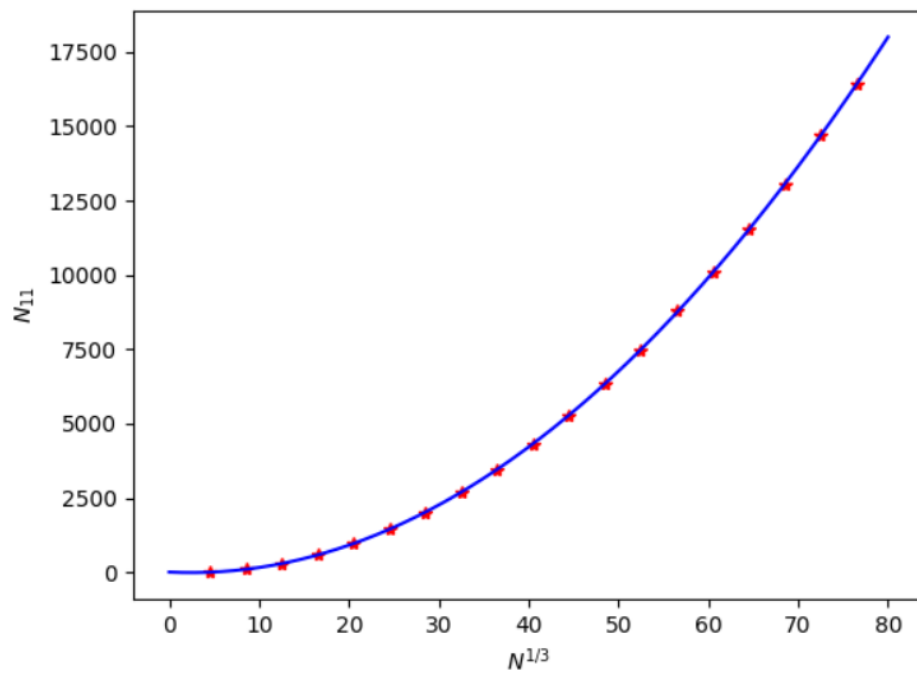


Figure 15: Figure 6: Same as Figure 4 for $z = 11$ for rhombic dodecahedral nanoparticles.

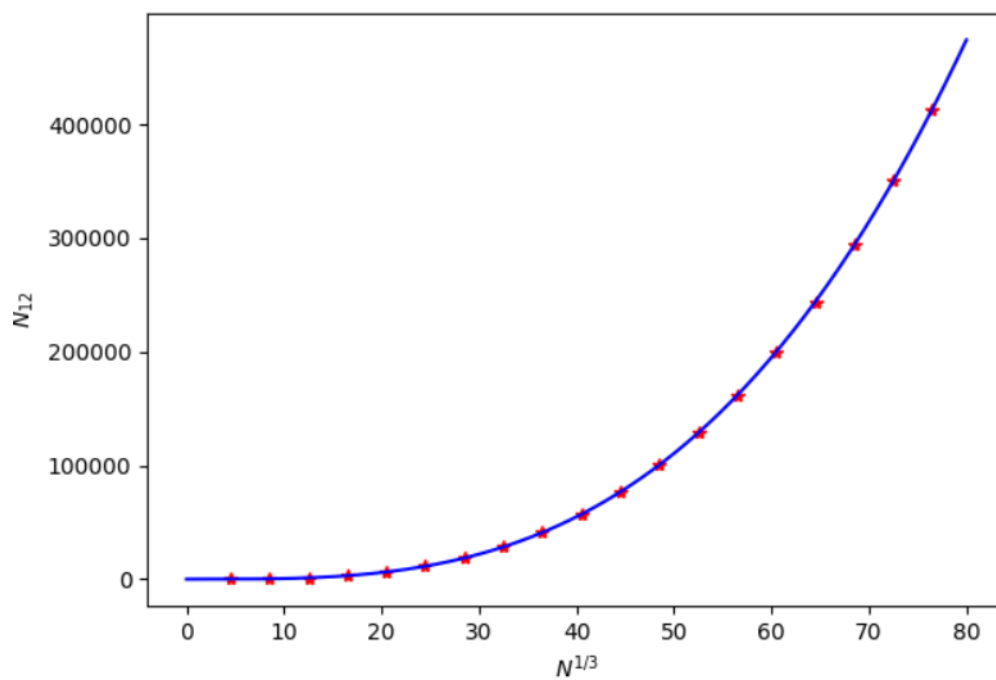


Figure 16: Same as Figure 4 for $z = 12$ for rhombic dodecahedral nanoparticles.

4 Surface energy calculations

The basic idea of Wulff construction is that the shape of a nanoparticle doesn't depend on the absolute values of surface energies but depends on the ratios between surface energies. In this chapter we present the formula we use in order to calculate the surface energy per unit area of Au(*hkl*) surfaces. We compare our results to a continuous model which is based on the geometry of the crystal and number theory. This model depends on the type of the interatomic potential used to describe the interactions between gold atoms.

4.1 Surface tension and surface energy

Surface tension is the property that liquid surfaces have in order to resist changes of their shape. Liquids have the tendency to take the shape that has the smallest possible surface. A typical example of this property of liquids is the shape of drops of water. In the absence of gravity, water drops have spherical shape as the sphere is the shape with the smallest surface-to-volume ratio. Surface tension symbolized by the Greek character γ and its dimensions is force per length.[22]

In solid-state physics, surface energy is the energy needed to form a surface of unit area parallel to (*hkl*) plane of the crystal. Surface energy is analogous of the surface tension of liquids and it expressed as energy per unit area. Surface energy is positive since it is the energy of creating “dangling bonds” at the surface. Bulk atoms have 12 neighbors but the atoms at the surface have less than 12. This means that in order to create a surface, bonds have been broken, so surface atoms have higher energy than bulk atoms. [23]

We can calculate the surface energy of a solid surface using a thick slab of the material where its surfaces are parallel to (*hkl*) plane. The thickness of the slab must be such that the atoms in the middle of the slab can be considered as bulk atoms. For such a slab, surface energy can be calculated as follows:

$$\gamma = \frac{E_{slab} - NE_{bulk}}{2A} \quad (13)$$

where E_{slab} is the energy of a slab composed of N layers, E_{bulk} is the energy of a bulk atom and A is the surface area. Due to the fact that a slab has 2 surfaces, its total area is $2A$. E_{bulk} can be calculated considering an atom in the unit cell of fcc crystal structure of the gold which is periodically repeated in three directions [19, 23-25]. In this work, we calculate the surface energy using the unit $eV/\text{\AA}^2$.

Figure 17 shows three low-index gold surfaces, (100), (110) and (111). These surfaces can be easily constructed using ASE. The atoms of (100) surface 8 nearest neighbors ($z = 8$) while the atoms of (110) and (111) surfaces have 7 and 9 nearest neighbors ($z = 7$ and $z = 9$) respectively. (111) surface has the highest coordination number thus the fewer “dangling bonds” and therefore we expect to have the lowest surface energy. On the other hand, (110) has the lower coordination number so the most “dangling bonds” consequently the highest surface energy. So we conclude in following inequality:

$$\gamma_{(111)} < \gamma_{(100)} < \gamma_{(110)} \quad (14).$$

The next step is the calculation of surface energies of these three low-index surfaces. In order to do this, we will use a Python code that simulates the slabs of (hkl) surfaces. A slab is a thick piece of the material consisting of layers of atoms of the material, in our case is gold. Here, we used slabs with different number of layers ($N = 2 - 10$). We also need to use an interatomic potential that describes the interactions between gold atoms. For this purpose, we will use the following four potentials:

1. (EAM-G). Embedded-Atom-Method (EAM) potential of Grochola et al. [26].
2. (EAM-O). EAM of Olsson et al. [27].
3. (LJ) Lennard Jones potential with $\epsilon = 0.4415 \text{ eV}$, $\sigma = 2.620 \text{ \AA}$ [28,29].
4. (MORSE). Morse potential with $D_0 = 0.4826 \text{ eV}$, $a = 1.6166 \text{ \AA}^{-1}$, $r_0 = 3.004 \text{ \AA}$ [28, 29].

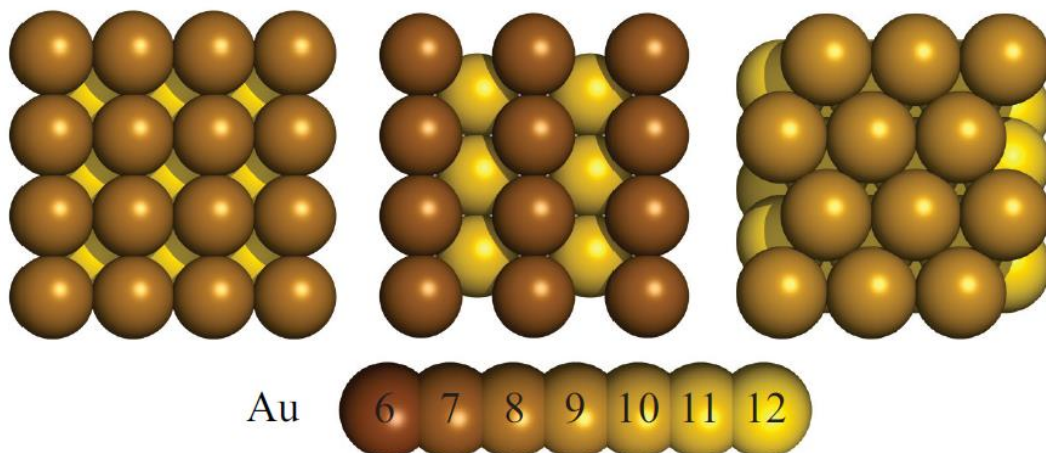


Figure 17: Top view of Au surfaces. Au(100) (left), Au(110) (center), Au(111) (right). Different colors indicate different types of atoms. [19]

Table 10: Surface energy of low-index gold surfaces using slabs with different number of layers and four different potentials. The unit of surface energy is $eV/\text{\AA}^2$.

Potential	N	$\gamma_{(111)}$	$\gamma_{(100)}$	$\gamma_{(110)}$
LJ	2	0.18000451	0.18512678	0.18219288
	3	0.18296489	0.19024102	0.19515284
	4	0.18325796	0.19111569	0.19914188
	5	0.18325796	0.19111569	0.20037091
	6	0.18325796	0.19111569	0.20069423
	7	0.18325796	0.19111569	0.20069423
	8	0.18325796	0.19111569	0.20069423
	9	0.18325796	0.19111569	0.20069423
	10	0.18325796	0.19111569	0.20069423
	MORSE	2	0.17353083	0.17825931
3		0.17394781	0.17956393	0.18949701
4		0.17395585	0.17962140	0.19070258
5		0.17395585	0.17962140	0.19083782
6		0.17395585	0.17962140	0.19085142
7		0.17395585	0.17962140	0.19085142
8		0.17395585	0.17962140	0.19085142
9		0.17395585	0.17962140	0.19085142
10		0.17395585	0.17962140	0.19085142
EAM-G		2	0.08275758	0.10093474
	3	0.07997601	0.090100622	0.11479495
	4	0.07993664	0.08974705	0.10867754
	5	0.07993664	0.08974705	0.10825963
	6	0.07993664	0.08974705	0.10821704
	7	0.07993664	0.08974705	0.10821704
	8	0.07993664	0.08974705	0.10821704
	9	0.07993664	0.08974705	0.10821704
	10	0.07993664	0.08974705	0.10821704
	EAM-O	2	0.05264005	0.06060776
3		0.05258190	0.06010701	0.06653170
4		0.05258183	0.06010417	0.06563779
5		0.05258183	0.06010417	0.06562299
6		0.05258183	0.06010417	0.06562292
7		0.05258183	0.06010417	0.06562292
8		0.05258183	0.06010417	0.06562292
9		0.05258183	0.06010417	0.06562292
10		0.05258183	0.06010417	0.06562292

Table 10 shows the results given by formula (13) for surface energy of (111), (100) and (110) surfaces using different number of layers. Firstly, the inequality $\gamma_{(111)} < \gamma_{(100)} < \gamma_{(110)}$ is confirmed regardless of the number of layers N and the potential we used. As N increases, the surface energy converges to a constant value that depends on the potential we used. Therefore, surface energy doesn't depend on the thickness of the slab but we

need to use slabs that have thickness above a certain threshold so that atoms which are not in the surfaces are equivalent to bulk atoms. For example, if we used a slab with two layers, all the atoms are located at the surface and there are no bulk atoms. For slabs with (111) or (100) surfaces, we need at least 4 layers while for slabs with (110) surface we need at least 6.

As mentioned in section 2, the shape of nanoparticles based on Wulff construction, we noticed that the shape of a nanoparticle doesn't depend on the absolute values of surface energies but their ratios. For this reason, we calculated the ratios of surface energy $\frac{\gamma_{(100)}}{\gamma_{(111)}}$ and $\frac{\gamma_{(110)}}{\gamma_{(111)}}$. Due to the fact that (111) surface has the lowest surface energy, we used it as denominator. In the Table 11, we have collected the surface energies and the corresponding ratios. We observe that the absolute values of surface energy using the pair potentials Lennard Jones and Morse are much higher than the calculated values of EAM potentials and the values from other works. For example, Barmparis et al. [18, 19] calculated the surface energies of (111), (100) and (110) surfaces are 0.43, 0.53 and 0.56 that are very close to the values 0.45, 0.54 and 0.57 of Holec et al. [30]. In both cases, Density Functional Theory was used for these calculations. For the ratios of surface energies, Barmparis et al. [18,19] found that the ratios $\frac{\gamma_{(100)}}{\gamma_{(111)}}$ and $\frac{\gamma_{(110)}}{\gamma_{(111)}}$ are equal to 1.23 and 1.29 while Holec et al.[30] found the values 1.21 and 1.26. Therefore, Lennard Jones and Morse are not suitable potentials to describe the interatomic interactions of gold while EAM potentials seems to give better results.

Table 11: Surface energy (in $eV/\text{\AA}^2$) of three low-index surfaces and their corresponding ratios for four different potentials.

Potential	$\gamma_{(111)}$	$\gamma_{(100)}$	$\gamma_{(110)}$	$\frac{\gamma_{(100)}}{\gamma_{(111)}}$	$\frac{\gamma_{(110)}}{\gamma_{(111)}}$
LJ	0.183	0.191	0.201	1.04	1.10
MORSE	0.174	0.180	0.191	1.03	1.10
EAM-G	0.080	0.090	0.108	1.12	1.35
EAM-O	0.053	0.060	0.066	1.14	1.25

4.2 Continuum surface energy

In the previous paragraph, we described the atomistic method of calculating surface energy of a (hkl) surface and we used it to calculate the surface energy of three low-index surfaces. Here, we will refer to a continuous surface energy calculation model and we will use it to calculate the surface energies of the same surfaces.

In 2014, Rosakis et al. developed a continuum model that can be used for the calculation of surface energy. Various interesting results of number theory for certain lattice problems were used to derive the model as well as the geometry of crystal had a key role in the model. According to this simple model, the surface energy density is given by the formula:

$$\gamma(\vec{n}) = -\frac{1}{4} \sum_{\vec{w} \in L \setminus \{0\}} |\vec{w} \cdot \vec{n}| \varphi(|\vec{w}|) \quad (15)$$

where L is the Bravais lattice, \vec{w} are the lattice vectors, φ is a pair interatomic potential that describes the interactions between the atoms of crystal, \vec{n} is unitary and perpendicular to the surface vector. Pair potential φ may have unrestricted range but must decay fast enough. The Lennard Jones and Morse are such potentials. [31]

A more complex formula gives the surface energy when interactions are described by Embedded Atom Method (EAM) potential. An EAM potential offers a much more realistic description of interaction in metals and is defined by three functions: the embedded energy, electron density and the pair potential. The total energy E_{tot} of an arbitrary arrangement of atoms is given by EAM as

$$E_{tot} = \sum_i F(\bar{\rho}_i) + \frac{1}{2} \sum_{i \neq j} \varphi(r_{ij}) \quad \text{and} \quad \bar{\rho}_i = \sum_j \rho(r_{ij}) \quad (16)$$

where F is an embedding function, namely the energy to embed an atom i in the combined electron density $\bar{\rho}_i$ which is contributed from each of its neighboring atoms j by an amount $\rho(r_{ij})$, $\varphi(r_{ij})$ is the pair potential function representing the energy in bond ij which is due to the short-range electro-static interaction between atoms, and r_{ij} is the distance between an atom and its neighbor for that bond [32]. Equation (15) for EAM potential is written as [33] :

$$\begin{aligned} \gamma(\vec{n}) = & -\frac{1}{2|\vec{n}|} \sum_{k=1}^{+\infty} k [F(\sum_{\substack{\vec{w} \in L \\ \vec{w} \cdot \vec{n} \leq k}} \rho(|\vec{w}|)) - F(\sum_{\substack{\vec{w} \in L \\ \vec{w} \cdot \vec{n} \leq k-1}} \rho(|\vec{w}|))] \\ & - \frac{1}{4} \sum_{\vec{w} \in L \setminus \{0\}} |\vec{w} \cdot \vec{n}| \varphi(|\vec{w}|) \quad (17) \end{aligned}$$

Formulas (15) and (17) are analogous to the well-known Cauchy-Born formula that calculates the bulk energy per atom:

$$W(F) = \frac{1}{2} \sum_{\vec{w} \in L \setminus \{0\}} \varphi(|\vec{w}|) \quad (18) .$$

We will compare the results of formulas (15) and (17) to the results of the atomistic simulation of the previous section which were presented in the Table 11. The huge advantage of the continuous surface model is that we don't need to simulate a slab but we can work with the well-known three-dimensional periodic bulk structure.

The next step is to check if these formulas give us reliable results for surface energies. We will use again the following potentials:

1. (EAM-G). Embedded-Atom-Method (EAM) potential of Grochola et al. [26].
2. (EAM-O). EAM of Olsson et al. [27].
3. (LJ) Lennard Jones potential with $\varepsilon = 0.4415 \text{ eV}$, $\sigma = 2.620 \text{ \AA}$ [28, 29].
4. (MORSE). Morse potential with $D_0 = 0.4826 \text{ eV}$, $a = 1.6166 \text{ \AA}^{-1}$, $r_0 = 3.004 \text{ \AA}$ [28, 29].

We use the same interatomic potentials in order to have the ability to compare these results with the previous ones. Here, it is very important to notice that these formulas contain infinite sums. This problem can be easily solved by using a cut off, that is a distance at which the interactions between two atoms is zero. Also, we will calculate the bulk energy of gold using Cauchy-Born formula and we will compare the result with the corresponding result using an atom in the unit cell which is periodically repeated in three directions.

Table 12 presents the results of our calculations. As we expected, Cauchy-Born formula gives the same results with the energy calculation of an atom in the unit cell and periodic boundary conditions. The basic idea of this chapter is to understand if this continuous model is a safe option for surface energy calculation. For this reason, we compare the results of Tables 11 and 12 for surface energy. The impressive accuracy of the eight decimal digit guarantees the accuracy of the model. We conclude that the model works quite well and give us reliable results for surface energy.

Table 12: The bulk energy of gold (in eV) calculated using either Cauchy-Born formula or an atom in the unit cell with periodic boundary conditions. The surface energy (in $eV/\text{\AA}^2$) of three low-index surfaces was calculated using formulas (15) for pair potentials and (17) for EAM potentials.

	W	E_{bulk}	$\gamma_{(111)}^{Ros}$	$\gamma_{(100)}^{Ros}$	$\gamma_{(110)}^{Ros}$
LJ	-2.72733014	-2.72733014	0.183257 96	0.191115 69	0.200694 23
MOR SE	-2.81533626	-2.81533626	0.173955 85	0.179621 40	0.190851 42
EAM- G	-3.92421786	-3.92421786	0.079936 64	0.089747 05	0.108217 04
EAM- O	-3.80999990	-3.80999990	0.052581 83	0.060104 17	0.065622 92

5 An atomistic model for bulk, surface, edge and vertex energy of nanoparticles

In the previous chapter we focused on surface energy calculations on low-index surfaces of gold using a classical atomistic calculation and a continuous model which proved to be quite effective.

The energies of forming an edge between two surfaces and a vertex between two edges is not taken into account in the Wulff construction. Unlike surface energy, there are not enough information in the literature for edge and vertex energies of gold. The main purpose of this work is the development of an atomistic model that, apart from bulk and surface energy, it will also calculate edge and vertex energy of a nanoparticle. This work comes to fill the gap in the theoretical studies of gold nanoparticles.

The model is based on simple assumptions and include parameters which depend on the shape of the nanoparticle. The energy per atom is calculated using 8 different potentials and the results are compared with results from other experimental and theoretical studies in order to select one or more potentials that fit better in our model.

5.1 Total energy of the nanoparticle: From continuous to atomistic

In this section, we review the theory of P. Rosakis and I. Remediakis for the decomposition of nanoparticle total energies into terms for bulk-, surface-, edge- and vertex energy. This method allows for direct calculations of all these energies of a metal using total-energy calculations for few nanoparticles of identical shape but different sizes. This is the only method that can be used to systematically extract edge- and vertex energies for metals. [34]

The total energy of the nanoparticles can be described by the relationship

$$E = Vb + A\gamma + L\tau + N_v v \quad (19)$$

where b :bulk-, γ :surface-, τ :edge-, v :vertex- energy, V :volume, A :area, L :total edge length and N_v : number of vertexes. As we mentioned before, a nanoparticle contains different types of atoms, with different coordination number, therefore with different energy per atom. We also can express the total energy of the nanoparticle as

$$E = N_b E_b + N_f E_f + N_e E_e + N_v E_v \quad (20)$$

where N_b, N_f, N_e, N_v are the total number of atoms at the bulk, facets, edges and vertices of the nanoparticle respectively. The total number of atoms is given by the expression

$$N = N_b + N_f + N_e + N_v \quad (21).$$

For large nanoparticles equations (19) and (20) should give same results. Obviously $E_v = v$. There is no obvious connection between the other terms and there is no unique way to connect them.

In order to relate the remaining terms of equations (19) and (20) we will assume that the volume per atom is the same for all atoms of the nanoparticle, either they are located at the bulk or at the surface. In the fcc crystal structure, the unit cell has 4 atoms and the volume of the unit cell is a_0^3 . Consequently, the total volume of the nanoparticle can be calculated by the formula

$$V = N \frac{a_0^3}{4} \quad (22)$$

where a_0 is the lattice constant of gold.

We introduce two new parameters to the problem so that we can connect the total area A and the total edges length L of the nanoparticle with the number of atoms. Quantities A and L can be described by the following equations

$$A = \alpha a_0^2 N^{2/3} \quad (23), \quad L = \lambda a_0 N^{1/3} \quad (24).$$

Parameters α and λ depend on the nanoparticle's shape. It can be easily demonstrated using equations (22), (23) and (24) that

$$\alpha = \frac{A}{2^{4/3} V^{2/3}}, \quad \lambda = \frac{L}{2^{2/3} V^{1/3}}.$$

Based on the above, we conclude that equation (19) can be written in the form

$$E = Nb + \alpha a_0 \gamma N^{2/3} + \lambda \alpha_0 \tau N^{1/3} + N_v v \Rightarrow$$

$$\frac{E}{N} = b + \alpha a_0 \gamma N^{-1/3} + \lambda \alpha_0 \tau N^{-2/3} + N_v N^{-1} v \quad (25).$$

For example, for a cubic nanoparticle, equation (7) becomes

$$\frac{E}{N} = b + 39.6367 \gamma N^{-1/3} + 30.8428 \tau N^{-2/3} + 8 N^{-1} v.$$

We use nanoparticles of the same shape (cube, octahedron and rhombic dodecahedron) and different sizes and we calculate for each nanoparticle the energy per atom E/N and then, according to equation (25), we make a fit of these values as a function of $x = N^{-1/3}$. This fit will give us the coefficients c_1, c_2, c_3 and c_4 of a polynomial of third degree which we can use to calculate the values of b, γ, τ and v of the particular atomistic arrangement in this nanoparticle, i.e. $\gamma_{111}, \tau_{(111)/(111)}, v_{(111)/(111)/(111)}$. The values b, γ, τ and v can be expressed as function of polynomial coefficients as following

$$v = \frac{c_1}{N_v}, \tau = \frac{c_2}{\lambda \alpha_0}, \gamma = \frac{c_3}{\alpha \alpha_0}, b = c_4 \quad (26).$$

Obviously, all different shapes of nanoparticles should yield same values of b .

Table 13: Number of vertices (N_v), number of faces (N_f) and parameters a and λ (equation(27)) for typical polyhedral that can be found as nanoparticle shape.

	Cube	Octahedron	Rhombic dodecahedron	Deltoidal icositetrahedron	Truncated octahedron
Faces	(100)	(111)	(110)	(211)	(100), (111)
N_v	8	6	14	26	24
N_f	6	8	12	24	14
L	$12a$	$12a$	$24a$	$24(3 - 1/\sqrt{2})a$	$36a$
A	$6a^2$	$2\sqrt{3}a^2$	$8\sqrt{2}a^2$	$6\sqrt{29 - 2\sqrt{2}}a^2$	$(6 + 12\sqrt{3})a^2$
V	a^3	$\frac{1}{3}\sqrt{2}a^3$	$\frac{16}{9}\sqrt{3}a^3$	$\sqrt{122 + 71\sqrt{2}}a^3$	$8\sqrt{2}a^2$
a	2.3811	2.296	2.1213	2.0105	2.1092
λ	7.5595	9.7132	10.3923	14.0837	10.1022

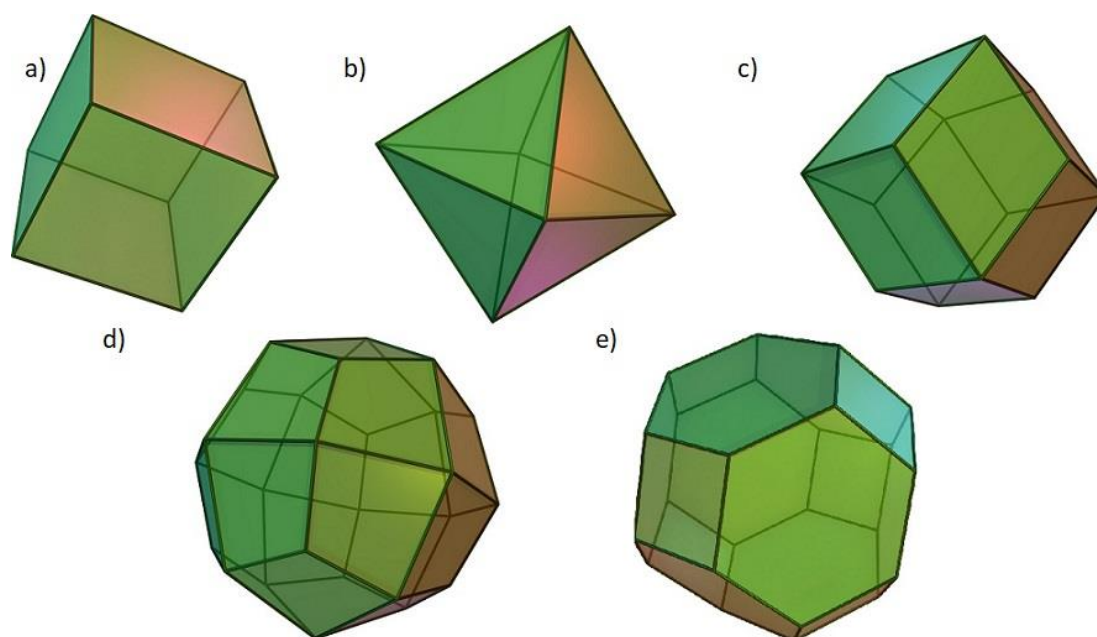


Figure 18: Typical polyhedra that can be found as nanoparticle shapes. a) Cube, b) Octahedron, c) Rhombic Dodecahedron, d) Deltoidal icositetrahedron, e) Truncated octahedron. Pictures taken from Wikipedia.

Figure 18 shows five typical shapes of nanoparticles, cube, octahedron, rhombic dodecahedron, deltoidal icositetrahedron and truncated octahedron. Most of them are nanoparticles containing one type of surfaces except one shape, truncated octahedron, that contains two types of surfaces. All useful

information and parameters for nanoparticles we need in this chapter are contained in the table 13. In this work, we focus on nanoparticles with high-symmetry.

5.2 Atomistic modeling of nanoparticles

We consider eight different interatomic potentials to describe the interactions between gold atoms. The LAMMPS program has been used to calculate the total energy of the nanoparticles. Apart from potentials supported by LAMMPS, we also used potentials from the Knowledgebase of Interatomic Models (KIM) project. We use models of nanoparticles with low index surfaces and then we will compare the results with other theoretical or experimental works. We used cubic nanoparticles ranging in size from 63 to 1073345 atoms, octahedral nanoparticles from 85 to 646899 atoms and rhombic dodecahedral nanoparticles from 93 to 447717 atoms and all of them created using ASE. The interatomic potentials we used are:

1. (EMT). The Jacobsen-Stoltze-Norskov Standard Effective Medium Theory (EMT) potential [36] as implemented in the ASAP code [37, 38].
2. (EAM-G). Embedded-Atom-Method (EAM) potential of Grochola *et al.* [26].
3. (EAM-Z). EAM potential of Zhou *et al.* [39].
4. (EAM-O). EAM of Olsson *et al.* [27].
5. (MORSE). Morse potential with $D_0 = 0.4826 \text{ eV}$, $a = 1.6166 \text{ \AA}^{-1}$, $r_0 = 3.004 \text{ \AA}$ [28,29].
6. (EAM-A) EAM of Ackland *et al.* [40].
7. (LJ) Lennard Jones potential with $\varepsilon = 0.4415 \text{ eV}$, $\sigma = 2.620 \text{ \AA}$ [28,29].
8. (EAM-F) EAM potential of Foiles *et al.* [41].

5.3 Discussion of results

The bulk energy of gold nanoparticles is independent of the nanoparticle's geometry. Both three shapes yield the same value of bulk energy shown in the first column of Table 14. Calculated bulk energies as given by different interatomic potentials don't show large deviation between them. Lennard Jones yields the highest value while EAM-Z and EAM-F the lowest value of the bulk energy. Morse, EMT, EAM-A and EAM-O are in a perfect agreement with the experimental value -3.81 eV . The calculated values of bulk energy are in a very good agreement with other DFT calculations of bulk energy such as the calculation of Souléde Bas *et al.* [15] and Keith *et al.* [42] who calculated the values -3.95 eV and -3.85 eV respectively.

Table 14: Results for bulk energy b (in eV) and surface energy γ (in $\text{eV}/\text{\AA}^2$) of (100), (110), (111) surfaces. The results were calculated using atomistic

simulation and fitting of eight different potentials. These results are compared with results of other computational methods and experimental works.

	b	$\gamma_{(111)}$	$\gamma_{(100)}$	$\gamma_{(110)}$	$\frac{\gamma_{(100)}}{\gamma_{(111)}}$	$\frac{\gamma_{(110)}}{\gamma_{(111)}}$
LJ	-3.65	0.170	0.178	0.187	1.04	1.10
MORSE	-3.81	0.171	0.177	0.188	1.03	1.10
EMT	-3.80	0.035	0.042	0.047	1.19	1.32
EAM-A	-3.79	0.039	0.050	0.054	1.28	1.39
EAM-Z	-3.93	0.058	0.068	0.077	1.16	1.31
EAM-F	-3.93	0.052	0.061	0.068	1.18	1.32
EAM-O	-3.81	0.053	0.060	0.066	1.14	1.25
EAM-G	-3.92	0.081	0.091	0.110	1.12	1.34
DFT	-3.95 ¹⁵ , -3.85 ⁴²	0.043	0.053	0.056	1.23	1.29
DFT-PBE³⁴		0.046 ¹⁹	0.053 ¹⁹	0.056 ¹⁹	1.15	1.22
DFT-LDA		0.065 ³⁵ , 0.079 ³⁰	0.087 ³⁵ , 0.084 ³⁰	0.097 ³⁵ , 0.089 ³⁰	1.34, 1.06	1.12, 1.13
DFT-GGA³⁰		0.045	0.54	0.57	1.21	1.26
FCD-GGA³⁰		0.080	0.102	0.106	1.27	1.33
Experimental	-3.81 ⁴³	0.094 ^{30,35} .				

In Figure 19 we plot the energy per atom E/N as a function of the total number of atoms of cubic nanoparticles using the interatomic potential EAM-G. We notice that as N increases, E/N decreases and this reduction is quite sharp. For very large N , the value of the energy per atom converges to $-3.92 eV/atom$ which is the calculated bulk energy using EAM-G. Bulk energy is the energy per atom we must give to each atom to remove it from the bulk of the nanoparticle and eventually decompose the nanoparticle.

Surface energy calculation of Au(hkl) has been of great interest to the scientific community. There are plenty of theoretical calculations of the surface energy of gold surfaces using DFT method. On the other hand, experimental determination of surface energy has limited to Au(111) surface. The results of our method are shown in Table 14. Except from the absolute values of surface energies, we also calculated the corresponding ratios which determine the shape of the nanoparticle.

First, we confirm the inequality $\gamma_{(111)} < \gamma_{(100)} < \gamma_{(110)}$. We notice that pair potentials Lennard Jones and Morse calculate the highest absolute values of surface energy, regardless the type of surface, compared to the other potentials and the experimental value; the surface energy of (111) surface is almost two times higher than experimental data. On the other hand, these potentials have the lowest ratios of surface energy.

EMT and EAM-A calculate the lowest absolute values of surface energy and the highest ratio $\frac{\gamma_{(110)}}{\gamma_{(111)}}$. Despite the fact that the surface energies which occur with the use of these two potentials are lower than experimental data, the results of EAM-A are very close to those of Barmparis et al. [18,19]. EAM-G calculate the values $0.081 \text{ eV}/\text{\AA}^2$, $0.091 \text{ eV}/\text{\AA}^2$ and $0.110 \text{ eV}/\text{\AA}^2$ for (111), (100) and (110) surfaces which are very close to the calculation of Holec et al.[30] and the experimental value $0.094 \text{ eV}/\text{\AA}^2$ [30,35].

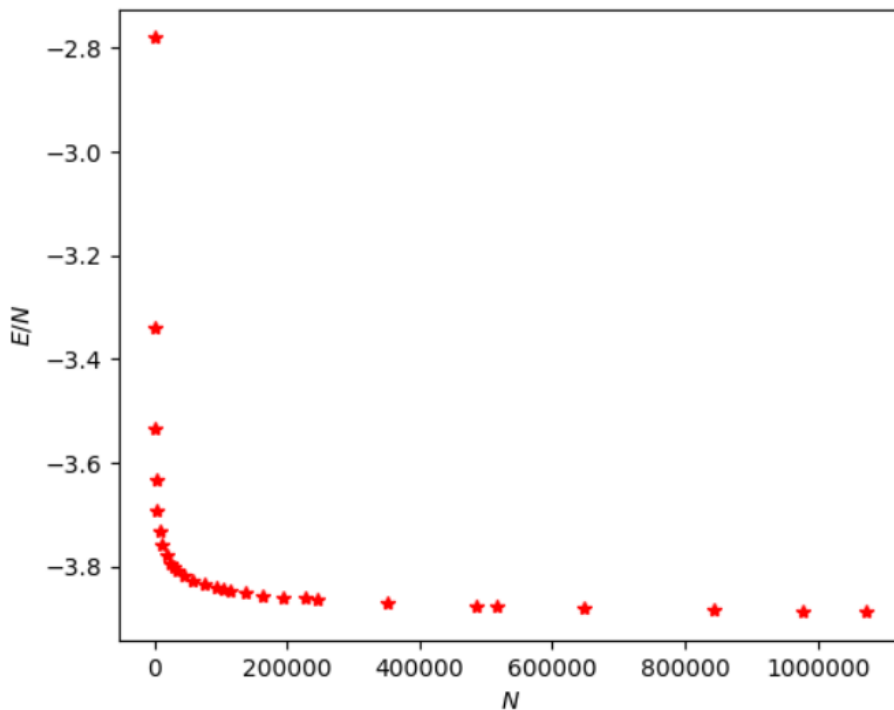


Figure 19: The energy per atom as a function of N for cubic nanoparticles using the interatomic potential EAM-G.

It is interesting how these values compare to surface energies obtained through slab models in the previous section. We will use the results are shown in the Tables 12 and 14. We notice that the values of bulk and surface energy of EAM-O are exactly the same. On the other hand, for Lennard Jones, Morse and EAM-G we observe small differences. For example, these potentials show a quite small deviation for surface energy. The calculated values of Cauchy-Born formula for Lennard Jones and Morse are about 1 eV smaller than the corresponding bulk energy obtained by atomistic model. This maybe is due to the cut off of these potentials in ASE.

Looking at ratios of surface energies, we observe that the surface energy values of the continuous model are identical to the corresponding values of formula (13) thus will compare the two last columns of Tables 11 and 14. We

used $\gamma_{(111)}$ as dominator in both cases because the (111) surface has the lowest surface energy. We don't expect any deviations between the ratios of EAM-O as the calculated values for two models are equal. But even for the other potentials where we noticed small deviations, the ratios don't present any significant difference. Thus, both methods can be used for surface energy calculations. The only difference is the required time for the calculation.: for the atomistic model, we need to calculate the energy per atom for several sizes of nanoparticles and in the case we use large nanoparticle this calculation can last from a few minutes to a few hours. On the other hand, the continuous model takes a few seconds but unfortunately it can only calculate the surface energy.

Table 15: Results for edge energy τ (in $\text{eV}/\text{\AA}$) for (100)/(100), (110)/(110), (111)/(111) edges as calculated using atomistic simulation and fitting with eight different potentials.

	$\tau_{(111)/(111)}$	$\tau_{(100)/(100)}$	$\tau_{(110)/(110)}$
LJ	-0.051	-0.126	-0.053
MORSE	-0.047	-0.111	-0.047
EMT	0.022	0.026	0.011
EAM-A	0.049	0.018	0.013
EAM-Z	0.072	0.073	0.048
EAM-F	0.040	0.046	0.021
EAM-O	0.025	0.026	0.015
EAM-G	0.132	0.144	0.065

Table 16: Results for vertex energy v (in eV) for (100)/(100)/(100), (110)/(110)/(110), (111)/(111)/(111) vertexes as calculated using atomistic simulation and fitting with eight different potentials.

	$v_{(111)/(111)/(111)}$	$v_{(100)/(100)/(100)}$	$v_{(110)/(110)/(110)}$
LJ	-0.205	0.166	0.053
MORSE	-0.187	0.149	0.060
EMT	0.031	0.111	0.119
EAM-A	0.026	0.507	0.299
EAM-Z	-0.095	0.246	0.152
EAM-F	-0.019	0.075	0.122
EAM-O	0.002	0.105	0.118
EAM-G	-0.657	-0.362	-0.019

Edge energy is the required energy to form an edge between two surfaces. As in the formation of surfaces, the formation of an edge requires the creation of "dangling bonds" and this leads to an increase in the energy of the atoms at the edges. We already know that the atoms at the edges have lower coordination number than bulk atoms and the atoms at the surfaces. Therefore, we expect edge energy to be positive value. In addition, the atoms at the edges of a cubic nanoparticle have less nearest neighbors than the corresponding atoms of octahedral nanoparticles so they have more "dangling bonds" per atom thus

$$\tau_{(100)/(100)} > \tau_{(111)/(111)} \quad (27).$$

Our prediction is reinforced by the fact that Lai et al. in his theoretical work calculate the energy of (100)/(100) and (111)/(111) using DFT method. For edges between (100) surfaces, they constructed a square prism and they applied periodic boundary condition along the longitudinal direction. On the other hand, the energy of edges between (111) surfaces calculated using an octahedron consisting of corners in addition to edges, surfaces and bulk atoms. They found that the edge energies are $0.178eV/\text{\AA}$ and $0.176eV/\text{\AA}$ for (100)/(100) and (111)/(111) edges respectively. [44]

Table 15 represents the results of our atomistic model for edge energy of cubic, octahedral and rhombic dodecahedral gold nanoparticles. Pair potentials Lennard Jones and Morse calculate negative edge energy. Therefore, these potentials don't describe quite well the interactions between atoms. On the other hand, the many body EAM and EMT calculate positive values for edge energies and regardless the potential, (110)/(110) edges have the lowest edge. EAM of Grochola et al. presents the highest edge energies which are closer to Lai et al.[44] calculation while EAM-A doesn't confirm inequality (27).

In Table 16, we see the summarized results for vertex energy. Unfortunately, we have no information from the literature so we know nothing about the sign on this quantity and we can't compare our results with other theoretical works. But the Table 16 can certainly give us some information about the potentials we can use in this atomistic model.

We mentioned earlier that pair potentials Lennard Jones and Morse calculated negative values for edge energy. In the case of vertex energy, Lennard Jones calculated the energies of the corner of the octahedral nanoparticle equal to $-0.205eV$ while for cubic and rhombic dodecahedral nanoparticles the corresponding values are $0.166eV$ and $0.053eV$. Morse calculated the vertex energies of the nanoparticle equal to $-0.187eV$, $0.149eV$ and $0.060eV$, respectively. Therefore, the vertex energy of octahedron is negative while the vertex energy of the other two shapes is positive. This fact further reinforces our claim that pair potentials are unsuitable for describing the interactions between gold atoms. EAM Zhou et al. and EAM Foiles et al. show similar behavior.

We thus conclude that the most efficient potentials to describe the interactions between gold atoms are EMT, EAM-O and EAM-G. Although EAM-G calculates edge energy in a very good agreement with Lai et al., the calculated values of vertex energy are negative. We could argue that the energy of a vertex of a nanoparticle is positive as vertices have the lowest coordination number so they have additional "dangling bonds". Unfortunately, we can't support this claim due to the lack of scientific data. On the other hand, we notice that (100)/(100)/(100) vertices have higher energy than (111)/(111)/(111) vertices using these four interatomic potentials. This can be easily explained

since the vertices of a cubic nanoparticle have lower coordination number than the vertices of an octahedral nanoparticle.

We understand that the coordination number of the atoms at the surfaces, the edges and the vertices of a nanoparticle play an important role in the energies of these positions. A rhombic dodecahedral nanoparticle is more complex than cubic and octahedral ones since the atoms of its outer shell has two possible coordination number depending their position. As a result, we can't compare the edge or vertex energy of a rhombic dodecahedral nanoparticle with the corresponding energies of cubic and octahedral nanoparticle.

6 Conclusions

Despite the fact that gold is chemically inert, it has been found that gold nanoparticles with size 1-5 nm are effective as catalysts. Some of the factors that affect their efficiency as catalysts are the shape, the size, the quantum size effects and the coordination number of the atoms.

In this work we focused on gold nanoparticles with low-index surfaces. We used cubic, octahedral and rhombic dodecahedral nanoparticles with several sizes, from small to very large sizes, to study the connection between the position of an atom and its coordination number. Then, we found formulas that calculated the number of atoms having a specific coordination number as a function of the total number of atoms of the nanoparticle. The number of atoms at the vertices is constant. On the other hand, the numbers of atoms at the edges and surfaces are linear functions of $N^{1/3}$ and $N^{2/3}$ respectively while the number of bulk atoms is approximately proportional to N . The efficiency of a nanoparticle as catalyst depends on its active sites density. As a nanoparticle increases in size, the fraction of atoms at the surfaces or edges decreases and the nanoparticle ceases to be effective in catalysis.

We calculated the surface energy of (111), (100) and (110) using gold slabs and four different potentials to describe the interactions between gold atoms. Surface energy is positive quantity because the atoms at the surfaces have lower coordination number than bulk atoms while (111) and (110) have the lower and the higher surface energy respectively. Then, we calculated surface energies of gold with an alternative continuous model which proved to be valid for this purpose. The results of the two models coincide up to eight decimals digits.

We developed a new atomistic model that calculates the energy per atom of the bulk, the surface, edge and vertex energy of the nanoparticle for the first time. We used 8 different potentials and we ended up to the following:

- As the total number of atoms increases, the energy per atom decreases and converges to the calculated bulk energy.
- This model calculates quite well the bulk energy of gold regardless the interatomic potential we used.
- All potentials except Lennard Jones and Morse calculate quite well the ratios of surface energies but only EAM-G calculate well the absolute values of surface energies of gold according to experimental data we have.
- The edge energy of (111)/(111), (100)/(100) and (110)/(110) edges calculated equal to $0.132 \text{ eV}/\text{\AA}$, $0.144 \text{ eV}/\text{\AA}$ and $0.065 \text{ eV}/\text{\AA}$ using EAM-G and this values are very close to other DFT calculations for gold.

- We have no information about the vertex energy of the nanoparticles. although EAM-G calculates quite well the bulk, surface and edge energy and it seems to be a very good interatomic potential to describe the interactions between atoms. On the other hand, we don't know if it calculates well the vertex energy because its values are negative and there are no other theoretical studies in order to compare our results.

This atomistic model gives us the ability to calculate in a very simple way two energies of the nanoparticle which we had not calculated until now, the edge and the vertex energy. Despite the simplicity of this model, it requires a lot of computing hours because of the very large nanoparticles required to have good fits.

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8 Supplementary Material

Gold nanoparticles of different shapes and sizes were constructed using ASE for the purposes of this study. Nanoparticles do not show imperfections and we add atoms at the edges to adjust their size. In chapter 2, we presented a theoretical about the number of atoms with coordination number z , where z depends on the shape but not the size of the nanoparticle. In this supplementary, we present the calculation of z and active sites density.

A. Cube

z	N_z	N_z/N_{tot}	n_z
3	8	12.7	645
5	12	19.05	967.
8	30	47.6	2420
12	13	20.6	1048
N_{tot}	63		

z	N_z	N_z/N_{tot}	n_z
3	8	2.19	111.3
5	36	9.86	500.7
8	150	41.1	2086.
12	171	46.8	2379
N_{tot}	365		

z	N_z	N_z/N_{tot}	n_z
3	8	0.73	37.
5	60	5.46	277.
8	366	33.3	1690.
12	665	60.5	3072.
N_{tot}	1099		

z	N_z	N_z/N_{tot}	n_z
3	8	0.33	16.5
5	84	3.42	174
8	678	27.6	1401
12	1687	68.7	3485
N_{tot}	2457		

z	N_z	N_z/N_{tot}	n_z
3	8	0.17	8.77
5	108	2.33	118.
8	1086	23.5	1190.
12	3429	74.04	3759.
N_{tot}	4631		

z	N_z	N_z/N_{tot}	n_z
3	8	0.102	5.20
5	132	1.69	85.8
8	1590	20.4	1033.
12	6083	77.9	3953
N_{tot}	7813		

z	N_z	N_z/N_{tot}	n_z
3	8	0.066	3.33
5	156	1.28	64.9
8	2190	18.0	912
12	9841	80.7	4097
N_{tot}	12195		

z	N_z	N_z/N_{tot}	n_z
3	8	0.045	2.26
5	180	1.00	50.86
8	2866	15.9	815.
12	14895	82.9	4208
N_{tot}	17967		

z	N_z	N_z/N_{tot}	n_z
3	8	0.03	1.60
5	204	0.81	40.89
8	3678	14.5	737.
12	21437	84.6	4297
N_{tot}	25327		

z	N_z	N_z/N_{tot}	n_z
3	8	0.027	1.37
5	216	0.73	37.
8	4110	13.86	703.5
12	25326	85.4	4335
N_{tot}	29660		

z	N_z	N_z/N_{tot}	n_z
3	8	0.02	1.18
5	228	0.66	33.6
8	4566	13.3	673
12	29659	86.07	4370
N_{tot}	34461		

z	N_z	N_z/N_{tot}	n_z
3	8	0.02	0.89
5	252	0.55	28.1
8	5550	12.2	618.
12	39753	87.2	4430
N_{tot}	45563		

z	N_z	N_z/N_{tot}	n_z
3	8	0.01	0.690
5	276	0.47	23.8
8	6630	11.27	572.
12	51911	88.2	4480
N_{tot}	58825		

z	N_z	N_z/N_{tot}	n_z
3	8	0.01	0.55
5	300	0.40	20.5
8	7806	10.5	532.
12	66325	89.1	4520
N_{tot}	74439		

z	N_z	N_z/N_{tot}	n_z
3	8	0.009	0.44
5	324	0.35	17.8
8	9078	9.80	498
12	83187	89.8	4560
N_{tot}	92597		

z	N_z	N_z/N_{tot}	n_z
3	8	0.008	0.40
5	336	0.33	16.6
8	9750	9.5	482.
12	92596	90.2	4580
N_{tot}	102690		

z	N_z	N_z/N_{tot}	n_z
3	8	0.007	0.36
5	348	0.31	15.6
8	10446	9.20	467.
12	102689	90.5	4590.
N_{tot}	113491		

z	N_z	N_z/N_{tot}	n_z
3	8	0.006	0.30
5	372	0.27	13.8
8	11910	8.67	440.4
12	12503	91.05	4620
N_{tot}	137313		

z	N_z	N_z/N_{tot}	n_z
3	8	0.005	0.25
5	396	0.24	12.2
8	13470	8.20	416.
12	150381	91.6	4650
N_{tot}	164255		

z	N_z	N_z/N_{tot}	n_z
3	8	0.004	0.21
5	420	0.22	11
8	15126	7.78	395
12	178955	92.	4670
N_{tot}	194509		

z	N_z	N_z/N_{tot}	n_z
3	8	0.004	0.18
5	444	0.2	9.88
8	16878	7.39	375.
12	210937	92.4	4691.
N_{tot}	228267		

z	N_z	N_z/N_{tot}	n_z
3	8	0.002	0.12
5	516	0.15	7.43
8	22710	6.44	327.
12	329251	93.4	4740
N_{tot}	352485		

z	N_z	N_z/N_{tot}	n_z
3	8	0.002	0.084
5	576	0.12	6.028
8	28230	5.82	295.
12	456336	94.06	4780
N_{tot}	485150		

z	N_z	N_z/N_{tot}	n_z
3	8	0.002	0.079
5	588	0.11	5.79
8	29406	5.71	290
12	485149	94.2	4780
N_{tot}	515151		

z	N_z	N_z/N_{tot}	n_z
3	8	0.001	0.063
5	636	0.098	5
8	34350	5.30	269.
12	612521	94.6	4803
N_{tot}	647515		

z	N_z	N_z/N_{tot}	n_z
3	8	0.001	0.048
5	696	0.083	4.19
8	41070	4.87	247.
12	800806	95.04	4830
N_{tot}	842580		

z	N_z	N_z/N_{tot}	n_z
3	8	0.0008	0.042
5	732	0.075	3.81
8	45390	4.65	236
12	930433	95.3	4840
N_{tot}	976563		

z	N_z	N_z/N_{tot}	n_z
3	8	0.0008	0.038
5	756	0.070	3.58
8	48390	4.51	229
12	1024191	95.41	4844
N_{tot}	1073345		

z	N_z	N_z/N_{tot}	n_z
3	8	0.0006	0.030
5	816	0.061	3.09
8	56310	4.19	213
12	1285676	95.7	4860.
N_{tot}	1342810		

B. Octahedron

z	N_z	N_z/N_{tot}	n_z
4	6	7.06	358.
7	36	42.4	2150.
9	24	28.2	1430
12	19	22.3	1130
N_{tot}	85		

z	N_z	N_z/N_{tot}	n_z
4	6	2.6	132
7	60	26	1320
9	80	34.6	1760
12	85	36.8	1870
N_{tot}	231		

z	N_z	N_z/N_{tot}	n_z
4	6	1.23	62.3
7	84	17.2	872.
9	168	34.4	1740
12	231	47.2	2400
N_{tot}	489		

z	N_z	N_z/N_{tot}	n_z
4	6	0.67	34.2
7	108	12.1	615.
9	288	32.3	1640
12	489	54.9	2790
N_{tot}	891		

z	N_z	N_z/N_{tot}	n_z
4	6	0.41	20.74
7	132	8.99	456.
9	440	30	1520.
12	891	60.6	3079.
N_{tot}	1469		

z	N_z	N_z/N_{tot}	n_z
4	6	0.27	13.5
7	156	6.92	351.
9	654	27.8	1405
12	1469	65.1	3307.
N_{tot}	2255		

z	N_z	N_z/N_{tot}	n_z
4	6	0.18	9.28
7	180	5.49	279
9	840	25.6	1300
12	2255	68.7	3490
N_{tot}	3281		

z	N_z	N_z/N_{tot}	n_z
4	6	0.13	6.65
7	204	4.46	226.
9	1088	23.7	1206.
12	3281	71.7	3640
N_{tot}	4579		

z	N_z	N_z/N_{tot}	n_z
4	6	0.1	4.93
7	228	3.69	187.
9	1368	22.1	1120
12	4579	74.1	3760
N_{tot}	6181		

z	N_z	N_z/N_{tot}	n_z
4	6	0.07	3.75
7	252	3.10	158
9	1680	20.7	1050
12	6181	76.1	3870
N_{tot}	8119		

z	N_z	N_z/N_{tot}	n_z
4	6	0.06	2.92
7	276	2.64	134.
9	2024	19.4	986
12	8119	77.9	3950
N_{tot}	10425		

z	N_z	N_z/N_{tot}	n_z
4	6	0.046	2.32
7	300	2.28	116
9	2400	18.3	928
12	10425	79.4	4030
N_{tot}	13131		

z	N_z	N_z/N_{tot}	n_z
4	6	0.037	1.87
7	324	1.99	101.1
9	2808	17.3	876.
12	13131	80.7	4098
N_{tot}	16269		

z	N_z	N_z/N_{tot}	n_z
4	6	0.030	1.53
7	348	1.75	88.9
9	3248	16.3	830
12	16269	81.9	4160
N_{tot}	19871		

z	N_z	N_z/N_{tot}	n_z
4	6	0.025	1.27
7	372	1.55	78.8
9	3720	15.5	787
12	19871	82.9	4209
N_{tot}	23969		

z	N_z	N_z/N_{tot}	n_z
4	6	0.021	1.07
7	396	1.38	70.31
9	4224	14.8	750
12	23696	83.8	4260
N_{tot}	28595		

z	N_z	N_z/N_{tot}	n_z
4	6	0.018	0.90
7	420	1.25	63.1
9	4760	14.1	715.
12	28595	84.6	4300
N_{tot}	33781		

z	N_z	N_z/N_{tot}	n_z
4	6	0.015	0.77
7	444	1.1	57
9	5328	13.5	684
12	33781	85.4	4340
N_{tot}	39559		

z	N_z	N_z/N_{tot}	n_z
4	6	0.013	0.66
7	468	1.02	51.7
9	5928	12.8	655
12	39559	86.1	4370
N_{tot}	45961		

z	N_z	N_z/N_{tot}	n_z
4	6	0.01	0.57
7	492	0.93	47.1
9	6560	12.4	628.
12	45961	86.7	4401.
N_{tot}	53019		

z	N_z	N_z/N_{tot}	n_z
4	6	0.0098	0.50
7	516	0.85	43.1
9	7224	11.9	603.6
12	53019	87.3	4430
N_{tot}	60765		

z	N_z	N_z/N_{tot}	n_z
4	6	0.009	0.44
7	540	0.78	35.6
9	7920	11.4	580.8
12	60765	87.8	4460.
N_{tot}	69231		

z	N_z	N_z/N_{tot}	n_z
4	6	0.008	0.39
7	564	0.72	36.5
9	8648	11.02	560
12	69231	88.2	4480.
N_{tot}	78449		

z	N_z	N_z/N_{tot}	n_z
4	6	0.007	0.34
7	588	0.66	33.8
9	9408	10.6	540.
12	78449	88.7	4503
N_{tot}	88451		

z	N_z	N_z/N_{tot}	n_z
4	6	0.006	0.31
7	612	0.62	31.3
9	10200	10.3	522
12	88451	89.1	4520
N_{tot}	99269		

z	N_z	N_z/N_{tot}	n_z
4	6	0.005	0.27
7	636	0.57	29.1
9	11024	9.94	504.5
12	99269	89.5	4540.
N_{tot}	110935		

z	N_z	N_z/N_{tot}	n_z
4	6	0.0049	0.25
7	660	0.53	27.1
9	11880	9.62	488.
12	110935	89.8	4560.
N_{tot}	123481		

z	N_z	N_z/N_{tot}	n_z
4	6	0.004	0.22
7	684	0.50	25.4
9	12768	9.32	473.
12	123481	90.2	4580
N_{tot}	136939		

z	N_z	N_z/N_{tot}	n_z
4	6	0.004	0.20
7	708	0.47	23.8
9	13688	9.04	459.
12	136939	90.5	4594
N_{tot}	151341		

z	N_z	N_z/N_{tot}	n_z
4	6	0.0036	0.18
7	732	0.44	22.3
9	14640	8.78	446
12	151341	90.8	4609
N_{tot}	166719		

z	N_z	N_z/N_{tot}	n_z
4	6	0.0033	0.17
7	756	0.41	21
9	15624	8.53	433.
12	166719	91.1	4620
N_{tot}	183105		

z	N_z	N_z/N_{tot}	n_z
4	6	0.003	0.15
7	780	0.39	19.7
9	16640	8.3	421.
12	183105	91.3	4640
N_{tot}	200531		

z	N_z	N_z/N_{tot}	n_z
4	6	0.0027	0.14
7	804	0.37	18.6
9	17688	8.08	410
12	200531	91.5	4650
N_{tot}	219029		

z	N_z	N_z/N_{tot}	n_z
4	6	0.0025	0.13
7	828	0.35	17.6
9	18768	7.86	399.
12	219029	91.7	4660
N_{tot}	238631		

z	N_z	N_z/N_{tot}	n_z
4	6	0.0023	0.12
7	852	0.33	16.7
9	19880	7.66	389.
12	238631	92.	4670.
N_{tot}	259369		

z	N_z	N_z/N_{tot}	n_z
4	6	0.0021	0.11
7	876	0.31	15.8
9	21024	7.47	379.
12	259369	92.2	4680
N_{tot}	281275		

z	N_z	N_z/N_{tot}	n_z
4	6	0.0019	0.10
7	900	0.3	15.01
9	22200	7.29	370.3
12	281275	92.4	4690
N_{tot}	304381		

z	N_z	N_z/N_{tot}	n_z
4	6	0.0018	0.093
7	924	0.28	14.3
9	23408	7.12	362
12	304381	92.5	4701.
N_{tot}	328719		

z	N_z	N_z/N_{tot}	n_z
4	6	0.0017	0.086
7	948	0.27	13.6
9	24648	6.96	353.
12	328719	92.7	4710.
N_{tot}	354321		

z	N_z	N_z/N_{tot}	n_z
4	6	0.0015	0.08
7	972	0.25	12.9
9	25920	6.80	345.
12	354321	92.9	4720
N_{tot}	409445		

z	N_z	N_z/N_{tot}	n_z
4	6	0.0015	0.07
7	996	0.24	12.3
9	27224	6.6	338
12	381219	93.1	4730
N_{tot}	409445		

z	N_z	N_z/N_{tot}	n_z
4	6	0.0014	0.069
7	1020	0.23	11.8
9	28560	6.51	330.3
12	409445	93.2	4735
N_{tot}	439031		

z	N_z	N_z/N_{tot}	n_z
4	6	0.0013	0.065
7	1044	0.22	11.3
9	29928	6.37	323.
12	439031	93.4	4740
N_{tot}	470009		

z	N_z	N_z/N_{tot}	n_z
4	6	0.0012	0.061
7	1068	0.21	10.8
9	31328	6.24	317
12	470009	93.6	4750
N_{tot}	502411		

z	N_z	N_z/N_{tot}	n_z
4	6	0.0011	0.057
7	1092	0.20	10.34
9	32760	6.11	310.1
12	502411	93.6	4760
N_{tot}	536269		

z	N_z	N_z/N_{tot}	n_z
4	6	0.0011	0.053
7	1116	0.20	9.91
9	34224	5.99	304
12	536269	93.8	4760
N_{tot}	571615		

z	N_z	N_z/N_{tot}	n_z
4	6	0.00099	0.050
7	1140	0.20	9.51
9	35720	5.87	298.
12	571615	93.9	4770
N_{tot}	608481		

z	N_z	N_z/N_{tot}	n_z
4	6	0.00093	0.047
7	1164	0.18	9.14
9	37248	5.75	292.
12	608481	94.1	4780
N_{tot}	646899		

C. Rhombic dodecahedron

z	N_z	N_z/N_{tot}	n_z
3	8	8.60	437
4	6	6.45	325
7	36	38.7	1965.
10	24	25.8	1310.
12	19	20.4	1037.
N_{tot}	93		

z	N_z	N_z/N_{tot}	n_z
3	8	1.30	65.8
4	6	0.97	49.4
5	24	3.89	197.
7	156	25.3	1284
10	48	7.78	395
11	96	15.6	790
12	279	45.2	2300
N_{tot}	617		

z	N_z	N_z/N_{tot}	n_z
3	8	0.41	20.8
4	6	0.31	15.6
5	48	2.45	125
7	372	19.01	965.
10	72	3.68	187
11	288	14.7	747.
12	1163	59.4	3017.
N_{tot}	1957		

z	N_z	N_z/N_{tot}	n_z
3	8	0.18	9.03
4	6	0.13	6.77
5	72	1.6	81.3
7	684	15.2	772.
10	96	2.13	108.4
11	576	12.8	650.3
12	3055	67.9	3450
N_{tot}	4497		

z	N_z	N_z/N_{tot}	n_z
3	8	0.093	4.71
4	6	0.070	3.53
5	96	1.11	56.5
7	1092	12.7	643.
10	120	1.39	70.7
11	960	11.1	565.
12	6339	73.5	3730
N_{tot}	8621		

z	N_z	N_z/N_{tot}	n_z
3	8	0.054	2.76
4	6	0.041	2.07
5	120	0.82	41.4
7	1596	10.8	551
10	144	0.98	49.7
11	1440	9.79	497
12	11399	77.5	3930
N_{tot}	14713		

z	N_z	N_z/N_{tot}	n_z
3	8	0.035	1.75
4	6	0.026	1.32
5	144	0.62	31.6
7	2196	9.48	481.
10	168	0.73	36.8
11	2016	8.71	442
12	18619	80.4	4082.
N_{tot}	23157		

z	N_z	N_z/N_{tot}	n_z
3	8	0.023	1.18
4	6	0.017	0.89
5	168	0.49	24.8
7	2892	8.42	428
10	192	0.56	28.4
11	2688	7.83	397.
12	28383	82.7	4200
N_{tot}	34337		

z	N_z	N_z/N_{tot}	n_z
3	8	0.016	0.84
4	6	0.012	0.63
5	192	0.38	20.
7	3684	7.56	385
10	216	0.44	22.5
11	3456	7.11	361
12	41075	84.4	4290
N_{tot}	48637		

z	N_z	N_z/N_{tot}	n_z
3	8	0.012	0.61
4	6	0.009	0.46
5	216	0.32	16.5
7	4572	6.88	350
10	240	0.36	18.3
11	4320	6.50	330.
12	57079	85.9	4360
N_{tot}	66441		

z	N_z	N_z/N_{tot}	n_z
3	8	0.009	0.46
4	6	0.007	0.35
5	240	0.27	13.8
7	5556	6.3	320.
10	264	0.3	15.2
11	5280	5.99	304.1
12	76779	87.1	4420
N_{tot}	88133		

z	N_z	N_z/N_{tot}	n_z
3	8	0.007	0.36
4	6	0.005	0.27
5	264	0.23	11.7
7	6636	5.82	295.
10	288	0.25	12.8
11	6336	5.55	282
12	100589	88.1	4480
N_{tot}	114097		

z	N_z	N_z/N_{tot}	n_z
3	8	0.006	0.28
4	6	0.004	0.21
5	288	0.2	10.1
7	7812	5.4	274.
10	312	0.22	10.9
11	7488	5.17	263
12	128803	89.	4520
N_{tot}	144714		

z	N_z	N_z/N_{tot}	n_z
3	8	0.004	0.23
4	6	0.003	0.17
5	312	0.17	8.78
7	9084	5.04	256
10	336	0.18	9.46
11	8736	4.84	246
12	161895	89.8	4560
N_{tot}	180377		

z	N_z	N_z/N_{tot}	n_z
3	8	0.004	0.18
4	6	0.003	0.14
5	336	0.15	7.70
7	10452	4.72	240
10	360	0.16	8.25
11	10080	4.55	231.
12	200219	90.4	4590
N_{tot}	221461		

z	N_z	N_z/N_{tot}	n_z
3	8	0.003	0.15
4	6	0.002	0.11
5	360	0.13	6.81
7	11916	4.44	225.
10	384	0.14	7.26
11	11520	4.29	218
12	244159	91	4620
N_{tot}	268353		

z	N_z	N_z/N_{tot}	n_z
3	8	0.002	0.13
4	6	0.002	0.095
5	384	0.12	6.07
7	13476	4.19	213
10	408	0.13	6.44
11	13056	4.06	206
12	294099	91.5	4650
N_{tot}	321437		

z	N_z	N_z/N_{tot}	n_z
3	8	0.002	0.11
4	6	0.002	0.08
5	408	0.10	5.44
7	15132	3.97	201.6
10	432	0.11	5.76
11	14688	3.85	196
12	350423	92	4470
N_{tot}	381097		

z	N_z	N_z/N_{tot}	n_z
3	8	0.002	0.09
4	6	0.001	0.07
5	432	0.095	4.9
7	16884	3.77	191.
10	456	0.10	5.17
11	16416	3.67	186.
12	413515	92.4	4690
N_{tot}	447717		