Icosahedral 13-Atom Gold Clusters: A Mathematical and Crystallographic Exercise

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Abstract

The small deviation of the outer shell gold atoms of a 13-atom icosahedral cluster from spherical atomic shape is calculated in order to compensate the mismatch between atomic radius of Au and circumsphere diameter of the icosahedron as limiting atomic distance. The density of the cluster is found to be a little bit greater than the density of face-centered cubic gold.

Keywords: Polyhedron, Platonic Solids, Mackay-Polyhedrons, Fibonacci Numbers, Volume-Area Ratio, Polyhedral Void Space**,** Density**,** Golden Mean.

1. Introduction

In 1962 Mackay reported about of a dense non-crystallographic packing of equal spheres and initiated the research on such icosahedral clusters [1]. The icosahedron belongs to the 5 *Platonic* solids [2] [3]. It is a convex regular polyhedron in three-dimensional *Euclidian* space and consists of 20 congruent equilateral triangular faces (*F*), 12 vertices (*V*) and 30 edges (*E*). These geometric elements obey the *Euler* relation $V + F - E = 2$ [4]. We are interested in the 13 atom cluster consisting of a first shell of 12 atoms of gold completed with an atom located at the center. Generally, the number of atoms building complete icosahedral clusters results in a series of special *Fibonnaci* numbers *C* according to

$$\boldsymbol{C(n)} = \frac{\mathbf{10}\boldsymbol{n}^{\mathbf{3}} - \mathbf{15}\boldsymbol{n}^{\mathbf{2}} + \mathbf{11}\boldsymbol{n} - \mathbf{3}}{\mathbf{3}} \quad (1)$$

One obtains for the first members

$$\boldsymbol{C(1) = 1 \quad C(2) = 13 \quad C(3) = 55} \quad (2)$$

Fibonacci numbers are derived and introduced by *Pisano* around the year 1202 [5].

More general we speak about *AuNCs* (Au nano-clusters). Their small size caused significant quantization to the conduction band leading to photonic properties and native luminescent properties allowing biomedical applications, for instance as therapy tool in cancer treatment [6]. However, in this contribution we deal with bar clusters without stabilizing ligand shells.
In the following we present a mathematical and crystallographic exercise for a better understanding of the important icosahedral clusters consisting of 13 gold atoms. We calculate the effective cluster diameter in comparison with the experimental value and the density of this cluster as well as the void space

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2. Properties of the Icosahedron

The icosahedron is a regular solid obeying non-crystallographic fivefold symmetry. The polyhedron notation is given by the symbol [$\boldsymbol{p_i^{F_i}}$], where *p* is the polygon multiplicity and *F* is the number of faces. The notation is **[3^{20}]**. Platonic solids can be drawn and dynamically visualized using for instance the software found under http://drajmarsh.bitbucket.io. However, the reader may construct the icosahedron with the help of coordinates for the vertices given in **Table 1**, where $\boldsymbol{\varphi}$ is the golden mean

$$\boldsymbol{\varphi} = \frac{\sqrt{5}-1}{2} = \mathbf{0.6180339887} \ldots \quad \boldsymbol{\Phi} = \frac{\sqrt{5}+1}{2} = \boldsymbol{\varphi}^{-1} = \boldsymbol{\varphi} + \mathbf{1} = \mathbf{1.6180339887} \ldots \quad (3)$$

But division of all coordinates by φ would transfer ± 1 to big $\pm\Phi = \pm\varphi^{-1}$ and ± φ to ± 1. These values were sometimes given in literature.

Table 1. Coordinates of Vertices for the Icosahedron and Pentagonal Dodecahedron
(Both solids are centered at the origin and suitably scaled for sake of simplicity)

Edge length: $a = 2\varphi$					
Regular icosahedron			**Regular pentagonal dodecahedron**		
x	*y*	***z***	*x*	*y*	***z***
0	± φ	± 1	± 1	± 1	± 1
± φ	± 1	0	0	± φ^{-1}	± φ
± 1	0	± φ	± φ^{-1}	± φ	0

Figure 1 illustrated the rotated icosahedron in order to show the fivefold axis. The central atom has a coordination of 12 in contrast to the shell atom with asymmetric 5 + 1 coordination. This means that the atoms at the two different positions should show slightly different properties.

Important geometric relations for the icosahedron are summarized below [7]. We use the notation V_p polyhedron volume, V_{sph} in-sphere volume, A_p polyhedron surface area, A_{sph} in-sphere area, r_{circ} circumsphere radius, r_i in-sphere radius, *a* polygon edge length.

$$V_p = \frac{5}{6}\varphi^{-2}a^3 = \mathbf{2.1816945 \cdot a^3} \quad (4)$$

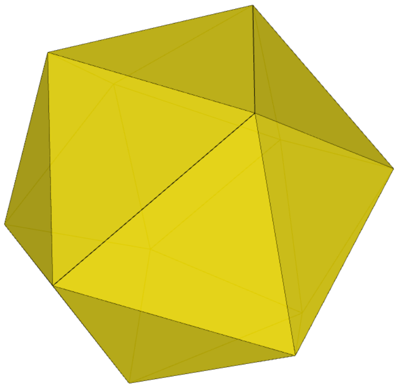

Figure 1. Illustration of an icosahedron showing one of the fivefold axes.

$$r_{circ} = \frac{\sqrt{3+\varphi}}{2}\, a = \mathbf{0.951056516 \cdot \boldsymbol{a}} \quad (5)$$

$$\approx \frac{a}{2} \cdot \left(15 - \frac{6}{\pi}\right)^{1/4} \quad (5a)$$

$$r_i = \frac{\varphi^{-2}}{2\sqrt{3}} a = \mathbf{0.755761313 \cdot \boldsymbol{a}} \quad (6)$$

$$V_{sph} = \pi \cdot \frac{\varphi^{-6}}{18\sqrt{3}} a^3 \quad (7)$$

$$\frac{V_{sph}}{V_p} = \pi \cdot \frac{\varphi^{-4}}{15\sqrt{3}} = \pi \cdot 0.263814507 = 0.8287977 \approx \frac{\pi}{2 \cdot 13} \varphi^{-4} \quad (8)$$

$$A_p = 5 \cdot \sqrt{3}\, a^2 = \mathbf{8.660254 \cdot \boldsymbol{a}^2} \quad (9)$$

$$A_{sph} = \pi \frac{\varphi^{-4}}{3} a^2 \quad (10)$$

$$\frac{A_{sph}}{A_p} = \pi \cdot \frac{\varphi^{-4}}{15\sqrt{3}} \approx \frac{\pi}{2 \cdot 13} \varphi^{-4} \quad (11)$$

$$\frac{V_p}{A_p} = \frac{\varphi^{-2}}{6\sqrt{3}} = \frac{r_i}{3} \quad (12)$$

3. The 13-Atom Gold Cluster

From the lattice parameter of face-centered cubic gold of $a_{fcc} = 4.0786$ Å we can obtain the atomic radius of gold

$$\boldsymbol{r_{Au}} = \frac{4.0786}{\sqrt{2}} \text{Å} = 1.442 \text{ Å} \quad (13)$$

However, a somewhat smaller parameter as developed from the cubic lattice parameter of gold may be possible due to the decrease of atomic radii with decreasing coordination number.
If we would have an icosahedral shell of only 12 gold atoms without a central atom, the cluster diameter would yield by applying $\boldsymbol{a} = 2\,\boldsymbol{r_{Au}}$

$$\mathbf{2}(\boldsymbol{r_{circ}} + \boldsymbol{r_{Au}}) = 2 \cdot (1.902113 + 1) \cdot \boldsymbol{r_{Au}} = 8.30\ \text{Å} \tag{14}$$

If the center is occupied to assemble a 13-atom cluster by maintaining the atomic volume of gold, the outer atomic shell suffer an atomic deformation from spherical to slightly pancake form to compensate for the mismatch caused by the fact that $\boldsymbol{r_{circ}}$ is a little bit smaller than $\boldsymbol{a}$ (equation 5). You can also follow the mismatch considering the in-sphere radius of the icosahedron $\boldsymbol{r_i}$, which is smaller than the high $\boldsymbol{h_T}$ of a tetrahedron as an example for a dense sphere packing

$$\boldsymbol{r_i} = \mathbf{0.755761313} \cdot \boldsymbol{a} \tag{15}$$

$$\boldsymbol{h_T} = \frac{\sqrt{6}}{3} \cdot \boldsymbol{a} = \mathbf{0.816496} \cdot \boldsymbol{a} \tag{16}$$

We proceed with the derivation of the small outer shell atomic deformation of a 13-atom icosahedral Au cluster. The formula for an elliptical deformed sphere with equal volume as the sphere is

$$\boldsymbol{V} = \frac{4\pi}{3} \boldsymbol{c_1^2 a^2} \cdot \boldsymbol{c_2 a} \quad \text{with} \quad \boldsymbol{c_2} = \frac{1}{c_1^2} \tag{17}$$

On can obtain a matching numerical result between the free halve-diagonal distance $\boldsymbol{r_{eff}}$ and the needed atomic space for an outer atom and the central atom

$$\boldsymbol{r_{eff}} = \boldsymbol{c_1} \cdot \mathbf{2}\boldsymbol{r_{Au}} \cdot \boldsymbol{r_{circ}} \tag{18}$$

$$\boldsymbol{r_{eff}} = \boldsymbol{c_2} \cdot \boldsymbol{r_{Au}} + \boldsymbol{r_{Au}} = \left(\mathbf{1} + \frac{1}{c_1^2}\right) \boldsymbol{r_{Au}} \tag{19}$$

Both equations result in a cubic equation with respect to the parameter $\boldsymbol{c_1}$

$$\boldsymbol{c_1^3} - \frac{c_1^2}{2r_{circ}} - \frac{1}{2r_{circ}} = \mathbf{0} \tag{20}$$

The solution provided for the ellipsoid axes parameters

$$\boldsymbol{c_1} = \mathbf{1.0255718} \tag{21}$$

and
$$\boldsymbol{c_2} = \mathbf{0.95075333} \tag{22}$$

Finally, we obtain matching distances

$$c_1 \cdot 2r_{Au} \cdot r_{circ} = 2.809085 \text{ Å} \tag{23}$$

$$c_2 \cdot r_{Au} + r_{Au} = \left(1 + \frac{1}{c_1^2}\right) r_{Au} = 2.809085 \text{ Å} \tag{24}$$

Then the cluster diameter d_{13} can be calculated to be

$$d_{13} = 4r_{Au}c_1r_{circ} + 2r_{Au}c_2 = 8.356 \text{ Å} \tag{25}$$

This result agrees well with the cluster diameter observed experimentally: $d_{13}(exp) = 84\ pm = 8.4$ Å [8].

4. Density Consideration

We ask what the density of the cluster is in comparison with crystalline gold. Gold crystallizes in the face-centered cubic crystal structure with lattice parameter $a_{fcc} = 4.0786$ Å and $Z = 4$ atoms in the unit cell, it has a calculated density D_x of

$$D_x = \frac{Z \cdot M}{V_u \cdot N_A} = \frac{4 \cdot 196.9665}{4.0786^3 \cdot 10^{24} \cdot 0.602214 \cdot 10^{-24}} = 19.2827 gcm^{-3} \tag{26}$$

where M is the molar weight and N_A is *Avogadro*'s number.
For the 13-atom gold cluster we obtain in a similar way by weighting the 12 shell atoms an effective Z

$$Z = \frac{12}{5} + 1 = 3.4 \tag{27}$$

$$a = 2 \cdot r_{Au} \cdot c_1 = 2.9537 \text{ Å} \tag{28}$$

$$V_p = 2.1817 \cdot a^3 = 56.217 \text{ Å}^3 \tag{29}$$

$$D_{Cluster} = \frac{Z \cdot M}{V_P \cdot N_A} = 19.781\ g \cdot cm^{-3} \tag{30}$$

It is no surprise that the 13-atom gold cluster is a little bit denser than crystalline gold. Interestingly, an approximate relation holds

$$D_{Cluster} \approx c_1 \cdot D_X \tag{31}$$

From a number theoretical view $\boldsymbol{c_1}$ can vice versa be approximated by

$$c_1 \approx \sqrt[3]{\frac{13}{12}} = 1.02704 \tag{32}$$

The volume ratio of the gold atoms to the icosahedron volume yields

$$\frac{V_{Au}}{V_P} = \frac{3.4 \cdot \frac{4\pi}{3} r_{Au}^3}{8 \cdot c_1^3 \frac{5}{6} \varphi^{-2} r_{Au}^3} = 0.756458 \tag{33}$$

and the void volume ratio respectively

$$1 - \frac{V_{Au}}{V_P} = 0.23542 \approx \varphi^3 = 0.2360679 \tag{34}$$

Comparable values for the face-centered cubic gold are

$$\frac{V_{Au}}{V_{fcc}} = \frac{4 \frac{4\pi}{3} r_{Au}^3}{16 \cdot \sqrt{2} \cdot r_{Au}^3} = \frac{\pi}{\sqrt{2} \cdot 3} = 0.74048 \tag{35}$$

$$1 - \frac{V_{Au}}{V_{fcc}} = 0.259519 \approx 1 - \sqrt[3]{2} = 0.259921 \tag{36}$$

It indicates again that the packing efficiency of the icosahedral cluster is higher than that for the face-centered cubic lattice.

Among the forces involved in the formation of such clusters, the driving out of the all-pervading vacuum energy field (*Casimir* force) must be named first [9].

5. Extended Applications

The photonic properties of icosahedral gold clusters with native luminescence have been successfully used in biomedical applications as therapy tool in cancer treatment [6]. Besides such applications, ligand stabilized icosahedral 13-atom gold clusters assembled in capillaries are conceivable to generate amplified spontaneous emission and lasing and would promise a quite stable facility. A recent example for such application is the generation of random lasing in capillaries doped with rhodamine 6*G*-microspheres [10].

5. Conclusion

The icosahedral cluster consisting of 13 atoms of gold is a very dense solid body and about 2.6 % denser than face-centered cubic gold. The 12 shell atoms deviate slightly from assumed spherical shape, in this way compensating the geometrical mismatch that is caused by the occupation of the center by an additional atom. The shell atoms can be approximated by an elliptically shaped influence sphere having two equal half-axes enlarged by the factor of 1.02557, and the third axis reduced by the factor of 0.95075. Since *Mackay*'s approach of non-crystallographic packing of spheres many important biomedical applications of such clusters with ever new possibilities have exceeded all expectations.

References

[1] Mackay, A. L. (1962) A dense noncrystallographic packing of equal spheres. *Acta Crystallographica* **15**, 916-918

[2] Archer-Hind, R. D. (1888) The Timaeus of Plato. *MacMillan and Co*, New York.

[3] Field, J. V. (1997) Rediscovering the Archimedean Polyhedra: Pierro della Francesca, Luca Pacioli, Leonardo da Vinci, Albrecht Dürer, Daniele Barbaro, and Johannes Kepler. *Archive for History of Exact Sciences* **50**, 241-289.

[4] Euler, L. (1752) Elemanta doctrine solidorum. *Novi commentarii academiae scientiarum imperialis petropolitanae* **4**, 109-160.

[5] Pisano, L. (1202) Fibonacci's Liber Abaci (Book of Calculation). Biblioteca a Nazionale di Firenze.

[6] Van de Looij, S. M., Hebels, E. R., Viola, M., Hembury, M., Oliveire, S., and Vermonden, T. (2021) Gold Nanoclusters: Imaging, Therapy, and Theranostic Roles in Biomedical Applications. *Bioconjugate Chemistry* **33**.

[7] Otto, H. H. (2021) Ratio of In-Sphere Volume to Polyhedron Volume of the Great Pyramid Compared to Selected Convex Polyhedral Solids. *Journal of Applied Mathematics and Physics* **9,** 41-56.

[8] Ren, Shi-Wei (2023) The deformation of the icosahedral gold 13-atom cluster. *Modern Physics Letters* B **8**,

[9] Casimir, H. B. G. (1948) On the attraction between two perfectly conducting plates. *Proceedings of the Koningklijke nederlandse Akademie van Wetenschappen* **B51**, 793-795.

[10] He, H., Russell-Hill, P., Blau, W. J., Kislyakov, I. M., Rosanov, N. N., Dong, N., and Wang, J. (2025) Amplified spontaneous emission and random laser generation in capillaries doped with rhodamine 6G-microspheres. *Applied Optics* **64**, 3383-3390.