Structural fuzziness of large gold clusters

Kuo Bao,1,2 Stefan Goedecker,2 Kenji Koga,3 Frédéric Lançon,4 and Alexey Neelov2

1 State Key Lab of Superhard Materials, Jilin University, Changchun 130012, China
2 Departement of Physics, Universität Basel, Klingelbergstr. 82, 4056 Basel, Switzerland
3 National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Ibaraki 305-8565, Japan
4 CEA, INAC, SP2M, Laboratoire de simulation atomistique (LSim), F-38054 Grenoble, France

The energetic ground state of gold clusters with up to 314 atoms consists of rather complicated geometries that have only a weak resemblance to the perfect icosahedra, decahedra and octahedra that are encountered for some magic numbers. The structure changes in most cases completely by the addition of a single atom. Other low energy structures are so close in energy that their Boltzmann weight is not negligible at room temperature.

Since the structure determines the functionality of any material, the knowledge of the structure is the first step to understand any property of a condensed matter system. Clusters are a particularly interesting system both scientifically and technologically. It is well known that for small clusters of less than 30 atoms the structure can drastically change by the addition of a single atom [1, 2, 3]. Size selected clusters offer thus the possibility to obtain a large variety of structures with possibly widely different functionalities. It has for instance been revealed that the reactive properties of Au20 depend on the exact form of the potential which is different from other gold clusters [4].

By applying global optimization methods to find the geometric ground state structure it has also been shown that the structures of small clusters are in most cases amorphous [2, 3, 5]. Global geometry optimization have been performed in a systematic way for up to 80 atoms [6] and for selected clusters up to 75 atoms [7]. For such a small number of atoms most clusters are amorphous, i.e. they have no well defined structure. This feature is independent of the exact form of the potential which is the Rosato Guillopé Legrand potential [7] (RGL) in our case, the Sutton-Chen potential in reference [8] or the Gupta potential in reference [9].

We extend these studies to much larger cluster sizes for which we no longer find amorphous ground state geometries. In order to determine the structure of large clusters containing a few hundred atoms, educated guesses of low energy structures were until now made instead of systematic global optimization. This procedure was used for metallic clusters in many publications. Both for model Lennard-Jones clusters [10] as well as for gold clusters described by various potentials [11, 12] they arrived all at the same conclusion. For small clusters icosahedral structures are energetically the lowest, for medium size clusters decahedral structures are best and for large clusters finally truncated octahedra. The reason for this evolution of the shape is that the ratio of surface to volume atoms is decreasing as the cluster size increases. Icosahedra are terminated everywhere with the energetically most favorable (111) surfaces and they are nearly spherical, but the internal atoms have a lot of strain. The truncated octahedra on the other hand have inside the perfect fcc crystalline structure but (100) facets with large surface energy. The decahedra have an intermediate behavior. The cluster sizes at which the transition between the different structures takes place depends on the element [13]. For gold the transitions happen already at rather small cluster sizes [4].

In this study we have obtained the structure of gold clusters with up to 300 atoms by global optimization using the minima hopping method [11, 12]. Minima hopping is a highly efficient global optimization method which can in particular reliably find the global minimum for multi-funnel landscapes. Since global optimization on the density functional level is not possible for such cluster sizes we have used the RGL interatomic potential with the parameters of reference [7], which has been widely used in studies of metallic clusters and turned out to be rather reliable. Fig. 1 shows the accuracy compared to density functional calculations for several configurations of a Au20 cluster. The errors are of the order of 1 eV which is a typical value for high quality force fields or tight binding schemes [3].

Fig. 2 shows the central result of our investigation, namely the energies of all the ground state configurations of the clusters for which we did a global geometry optimization together with their structure type. We distinguish the following structure types illustrated in Fig. 3

- Amorphous: No detectable structure
- Five fold symmetry (5-fold): A significant subset of atoms has one 5-fold symmetry axis. Marks Decahedra fall into this class as the special case where the subset comprises all the atoms of the cluster. The large majority of our structures are imperfect in the sense that the whole cluster is not invariant under rotations around the 5-fold axis.
- Single fcc (s-fcc): The cluster can be cut out of a fcc crystal. Perfect octahedra and truncated octahedra fall into this class as a special case.
- Twinned fcc (t-fcc): The cluster consists out of two fcc pieces ‘glued’ together. Twinned octahedra where the two parts are joined together after
FIG. 1: Comparison of the density functional (DFT) and RGL force field (FF) energies for relaxed configurations. The geometry relaxation with the RGL potential did only slightly change the stable DFT structures. The DFT configurations were obtained by doing Minima hopping with a density functional program [13]. If all the data points were on the dashed line we would have perfect agreement between DFT and FF for the energy differences between different structures.

a rotation have been introduced by Raoult [8] and later examined by Cleveland [14] who came to the conclusion that they are energetically not particularly favorable. In our case the structures are in most cases not octahedrons but more irregular structures, that just contain a microtwin. Structures of this type have according to our knowledge not been reported in the literature up to now.

The excess energy to form a cluster out of atoms in the perfect crystal relative to the number of surface atoms is denoted by $\Delta$ and defined as [15]

$$\Delta = \frac{E(N) - N\epsilon_{coh}}{N^{2/3}} \quad (1)$$

$E(N)$ is the energy of the cluster of $N$ atoms and $\epsilon_{coh}$ the cohesive energy per bulk Au atom. All energies are calculated with the RGL potential.

Perfect icosahedra (Ih), Marks-decahedra (M-Dh) and truncated octahedra (TOh) exist only for certain magic numbers. Our global optimization results of Table I show that even in the case where a gold cluster has a magic number of atoms, the global minimum is frequently not this perfect structure. In the case where the global minimum is one of the perfect structures listed in Table I it is not or not much lower in energy than less symmetric neighboring structures (Fig. 2).

Our results show that in most cases the structure of clusters that differ just by a single atom is completely different. Thus the rule that every atom counts is not only valid as hitherto believed for small clusters of a few dozen atoms that have amorphous structure but even for clusters of a few hundred atoms. Fig. 4 shows an example where the structure changes from 5-fold to s-fcc and t-fcc by the consecutive addition of atoms. Even in cases where the basic structure type (5-fold, s-fcc, t-fcc) is not modified by the addition of a single atom on its surface, whole regions change their structure and the shape of a cluster changes in general.

### Table I: Energies of perfect magic number structures relative to the energy of the global minimum of the cluster with the same number of atoms found by global optimization. A energy of 0. indicates that the perfect structure is the global minimum. The indexing of the M-Dh is the one from ref [1].

| Number of atoms | Magic number type | Global minimum type | Relative energy (eV) |
|-----------------|-------------------|---------------------|---------------------|
| 13              | Ih (1 shell)      | identical           | 0.                  |
| 38              | TOh (4,1)         | 5-fold              | 0.04                |
| 49              | M-Dh (2,1,2)      | identical           | 0.                  |
| 55              | Ih (2 shells)     | s-fcc               | 0.68                |
| 55              | TOh (5,2)         | s-fcc               | 1.22                |
| 75              | M-Dh (2,2,2)      | identical           | 0.                  |
| 79              | TOh (5,1)         | identical           | 0.                  |
| 101             | M-Dh (2,3,2)      | identical           | 0.                  |
| 116             | TOh (6,2)         | s-fcc               | 0.41                |
| 140             | TOh (6,1)         | identical           | 0.                  |
| 146             | M-Dh (3,2,2)      | identical           | 0.                  |
| 147             | Ih (3 shells)     | 5-fold              | 1.85                |
| 147             | TOh (7,3)         | 5-fold              | 2.49                |
| 192             | M-Dh (3,3,2)      | identical           | 0.                  |
| 201             | TOh (7,2)         | 5-fold              | 0.007               |
| 309             | Ih (4 shells)     | 5-fold              | 3.64                |
| 314             | TOh (8,2)         | identical           | 0.                  |
If clusters that differ only by one atom would in general have similar structures one could in most cases obtain the global minimum structure of the $N-1$ atom structure by taking away a weakly bound atom of the $N$ atom global minimum structure. We have done this test and could obtain the $N-1$ ground state only in 48 cases out of 203. One such case is shown in Fig. 5.

It is well known that it is difficult to establish a relation between theoretical ground state structures and experimental results since in many cases the structure of clusters is determined by the kinetics of the growing process rather than by the energetics. Even if one assumes that thermodynamical equilibrium has been obtained in an experiment, relating experimental results to simulation results is not straightforward. The size of the clusters prepared for diffraction experiments can neither be controlled up to a single atom, nor can the size be measured after the growth of the cluster with single atom accuracy in most cases. Therefore one has experimentally distributions of cluster sizes around a certain number of atoms. An additional factor that has to be considered is the fact that the energy separation between the geometric ground state and the second lowest local minimum structure is very small. Fig. 6 shows this energy difference for all our structures. It is of the order of the ambient thermal energy ($k_B T = 0.025$ eV) and therefore at room temperature not only the global minimum will be encountered but also a few other low energy configurations. Similar small energy differences were also found for a few selected small gold clusters by Soler et al. [16] and for silicon clusters by Hellmann et al. [17] using rather accurate density functional and Quantum Monte Carlo methods. The existence of a large number of structures that are energetically very close to the global minimum is also illustrated by the fact that within an energy interval of .1 eV above the global minimum there are on average 12 configurations for the clusters studied in this work. All these facts show that in experiment one can not expect to observe a single structure but rather a distribution of structures as it is indeed the case [18, 19].

Like for silicon clusters [17] it is expected that entropy effects can change the energetic ordering, i.e. the order given by the free energy at room temperature or somewhat above is different from the energetic ordering at zero temperature. Highly symmetric configurations become disfavored with respect to less symmetric configurations at finite temperatures. We found many low symmetry configurations that are very close in energy to high symmetry global minimum configurations. For the M-Dh

FIG. 3: Illustration of our classification of the various cluster structures. One row always shows the different perspectives (along x, y and z) axis of the same cluster. In the case of the 5-fold structure the atoms on the 5-fold axis are shown in grey instead of black. In the case of the t-fcc structure the atoms in the twin plane are shown in grey.

FIG. 4: The global minimum structure of Au91 (5-fold), Au92 (s-fcc) and Au93 (t-fcc)

FIG. 5: The global minima structure of Au62 is shown on the left hand side. Taking away a weakly bound atom (shown in grey), we get the global minima of Au61 shown on the right hand side.
Au_{192} cluster (Table I) there is for instance another configuration that is only 0.04 eV higher in energy and which has only one mirror plane. Even though this small energy difference is certainly not reliable given by the RGL potential it is to be expected that DFT or even Quantum Monte Carlo calculations would give low symmetry configurations that are very close in energy to certain high symmetry configurations.

The fact that taking out a single or a few atoms in our global geometry optimization induces a structural change can also be understood by a geometric argument. All our low energy structures have the property that they have rather smooth surfaces. Taking out one or several atoms will at some point lead to non-smooth surfaces that have steps or holes and thus to cluster shapes that are energetically unfavorable.

The structures of the ground state and the first excited configuration are available as supplementary material. We thank the Swiss National Science Foundation and the CSC (China Scholarship Council) for the financial support of our research work and the CSCS for computing time.

**FIG. 6:** The energy difference between the global minimum and the second lowest local minimum for all the clusters studied. If both minima share the same structure, this is indicated by a cross symbol (+); otherwise by a times symbol (×). For Au_{55} we have for instance an amorphous structure, previously proposed to be the ground state [5], which is only .014 eV higher in energy than our ground state.

Given the fact that the error bars of the RGL potential are larger than the energy differences between the global minimum structure and other low energy structures we can certainly not claim that the global minima structures that we found are the true global minimastructures. What is however true and does not depend on the form of the interatomic potential is that there exist completely different types of structures that are very close in energy. This is due to the fact that a cluster can not satisfy all the conditions that would lead to a lowering of the energy, namely a small surface area, mainly (111) surfaces, few grain boundaries and little strain in a fcc like core region. Favoring one condition at the expense of another gives similar energies.

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