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ReaxFF Molecular Dynamics Simulations of Large Gold Nanocrystals

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Abstract

A systematic study of gold nanocrystals is carried out using Molecular Dynamics simulations with reactive force fields. The nanocrystal size is varied between 2 and 10 nm with methane and butane thiolate as ligands. The reactive force fields allow to investigate the formation of staples. The simulations explain several experimental observations such as the number of staples per thiolate of about 40 % and the occupation of the top adsorption sites on the facets. They also show that the frequency of staples is increased on the edges which leads to a desorption of gold atoms from the nanocrystal edges. In contrast to previous non reactive simulations, no difference between the distances of the ligands on the nanocrystal edges and facets is observed. Except for the 2 nm particles, the nanocrystal size and the alkane chain length of the ligands have only a small influence on the nanocrystal properties. The occupation of adsorption sites and staple frequencies are very slowly converging properties taking more than ns.

1. Introduction

Metallic nanoparticles have specific properties which make them interesting for many applications.¹⁻³ Thus, gold nanoparticles are used in thermal cancer therapy² and for biosensors.³ To avoid nanoparticle agglomeration, they are usually coated with ionic or polymeric ligands such as thiolates. These ligands adsorb on the nanoparticle surface to form a protective monolayer.

For thiolates, the ligands adsorb with the sulfur heads and form self-assembled monolayers (SAMs) which were widely studied on flat gold, silver and copper surfaces by experiment and theory.^{4,5} In the case of gold, alkanethiolates form hexagonal superlattice, but also more complex structure such the 2x4 lattice have been observed.⁴⁻⁶ Theoretical calculations predicted the formation of RS-Au-SR staples with the formation of adatoms and vacancies.^{5,6} These predictions were confirmed by several experiments.^{7,8} It shows that the gold surface may markedly reorganize due to the presence of ligands which was also confirmed by Tight-binding DFT and reactive force field simulations.⁹⁻¹³

The “three-dimensional” SAMs of alkanethiolates on the surface of gold nanocrystals (NCs) have also been widely studied by experiments¹⁴⁻¹⁷ and simulations.¹⁸⁻²³ The experiments show some specific differences with respect to planar gold surfaces such an about 10 % higher surface coverage and a higher reactivity. The surface coverage has been explained by the formation of a new SAM on the edges of the NC facets.^{22,23} However, previous atomistic simulations on gold NCs neglect the possibility of a dissociation of Au-Au bonds and thus, strongly reduce the motion of gold atoms. This may explain why the formation of staples is not observed in these simulations, which is in contrast to the results of DFT calculations on small NCs.⁷

The aim of this article is to use reactive force fields of the ReaxFF type^{12,13,24-29} to study the SAMs of methane and butane thiolates on gold NCs up to a size of 10 nm. The ReaxFF proposed by Monti et al.²⁸ has been used. Actually, ReaxFF will allow us to study the formation of staples which are molecular species the formation of which cannot be correctly modeled by usual force fields. We will show that for nanoparticles, the reorganization of the gold surface and the formation of staples play a very important role.

Methane thiolates are studied here, since they have been widely used on gold surfaces. We choose it to compare to the results previously obtained on planar surfaces.^{4-6,13,26} Butanethiol is a "real" ligand for nanoparticles even when octane and dodecanethiol are more frequently used.¹ Since the calculations are very time consuming we have to restrict our calculations to

these small thiolates. It should be noted that previous simulations^{23,24} show that the length of the alkanethiolate does not markedly influence the results, which agrees to the observations obtained in this article.

We chose to study octahedral nanoparticles. It should first be noted that octahedral nanocrystals are really observed in experiments.¹ However, truncated octahedra are more often found. We decided nevertheless to study octahedra, since their surface is only made of Au(111) surfaces and edges between these. Thus, their properties can be interpreted with respect to a single type of surface, which is not the case of truncated octahedra made of different surface types. Moreover, the large facets enable us to investigate the transition between the behaviors observed on flat surface and on NCs.

Previously,^{18,23,24} the atomistic simulations of nanoparticles started with the nude nanocrystals surrounded by the ligands. In the first part of the simulations the ligands adsorb on the NC to form the SAM which were then analyzed. We will show here that this procedure does not work in the case of reactive force fields. We solved this technical issue by creating a new tool which transfers SAMs on the NC surface. These initial configurations can then be used to set up simulations. Moreover, we created new analysis tools, since the existing ones are based on the hypothesis that the gold atoms do not move.

In this paper, we will first present the used ReaxFF for the gold-thiolate system and discuss its reliability. Then, the simulation method and the new set-up and analysis tools are presented. In the following, the simulations runs are analyzed. First, the change of the nanocrystal morphology due to the staple formation is investigated. Then, the occupation of the adsorption sites is studied. Finally, the staple formation and distance between the ligands are analyzed. For all results, we discuss the reliability of the calculated properties followed by a study of their evolution as a function of alkane chain length and nanocrystal size.

2. Methods

2.1. The ReaxFF model

The ReaxFF formalism used here is presented in the articles by van Duyn et al.^{30,31}

This force field allows bond breaking and formation, as all the contributions except of the van der Waals and electrostatic terms are expressed as a function of the bond order. Atomic charges are calculated by the *Electronegativity Equalization Method*.^{32,33}

For gold-thiolate systems three different parameter sets have been proposed.^{12,24-29} These ReaxFF use the same Au-Au interaction proposed by van Duyn et al., but different parameters

for the interaction of gold with the other atoms. In a recent paper,¹³ the properties obtained by these force fields were compared to DFT results in the case of an Au₂₀ tetrahedron. All ReaxFF do markedly overestimate the distances between the atoms on the edges of the cluster. It was shown that the ReaxFF proposed by Monti et al. correctly reproduce the adsorption geometries and energies. It should be noted that this force field favors the bridge sites on the edges of the clusters in comparison to the DFT calculations. In this study the ReaxFF proposed by Monti et al.²⁸ is used. This was the only possible choice, since the other force fields do not lead to a staple formation in contradiction with experiments as shown previously.¹³

2.2. Simulation methods

The LAMMPS program is used to perform the Molecular dynamics simulations in the NVE ensemble.^{34,35} In all the molecular dynamics (MD) simulations a time step of 0.25 fs is applied. To assure a correct equilibration the temperature was slowly increased from 0 to 300 K during 300 000 steps using the Berendsen's thermostat (damping constant of 5 fs). The simulation was then continued for 8 million steps (2 ns) at 300 K and the last 800000 configurations obtained by these runs were analyzed and averaged. We observed that the occupation frequencies of adsorption sites and the number of staples are slowly converging, which demands long runs of more than one ns.

2.3. Setup and Analysis tools

As explained in the introduction, two python programs were added to our home-made NATOMOS package, which enables the set-up and analysis of nanoparticle simulations.

The new program ntm_setup.py is used for the set-up of nanoparticle simulations. It defines the initial positions of the atoms in the simulation box. Details of the program are explained in the SI.

Four different ways are used here to set up the initial position of the ligands:

- For the SAM configuration a self-assembled monolayer of thiolates on Au(111) obtained by Groenbeck et al.³⁶ (configuration 1 in Figure 1 of this article) is projected on the nanocrystal surface.
- For the EDGE configuration the same SAM as before is taken for the facets, but a different SAM is employed on the edges. The sulfur S atoms are put on a bridge position between two neighboring gold atoms on an edge. The backbone of the alkane chains are positioned perpendicular to the edges.

- For the RANDOM configuration the S atoms of the thiolates are positioned randomly on the NC surface. The coordinates of the other ligand atoms relative to the head atom are taken from a file.
- For the ZIGZAG configuration the coordinates of the S and C atoms of the thiolates are obtained by previous non-reactive simulations.²³ The hydrogen atoms are added respecting the usual geometry of CH₂ and CH₃ groups.

The program ntm_ana.py analyzes the files obtained at the end of the simulations.

First, the number of neighbors of the gold atoms are determined which shows if the geometry of the gold nanocrystals has changed during the simulation. Then the number and position of adsorbed thiolate and the occupation of adsorption sites is evaluated. Finally, the distance between neighboring S atoms and the number of staples are calculated as a function of the adsorption position. Details of the program are explained in the SI. Also the programs are given in the supporting information with an explanation how to use them.

All results obtained by the analysis and shown in the figures are given in the tables S1 to S10 in the Supporting Information.

Please note that we restrict our analysis mainly to the properties observed on the edges and centers of the facets, since those on the vertices cannot be determined with enough precision.

3. Results and Discussions

3.1. Preliminary simulations

In previous simulations,^{18,20,22,23} the adsorption of thiolate on nanocrystals has usually been studied starting with a random initial configuration of the ligands. In this case, the ligand molecules are put on random positions and orientations in the simulation box, while the nanocrystals without ligands are positioned in the center of the box. We have carried out simulations with these initial configurations for HSM_e and SM_e. In both cases, we observed that the ligands adsorb mainly with the methyl group in contrast to experiments and previous simulations (see Figure S1 in SI). This shows that this method cannot be used here to study the thiolate adsorption by the S atom. For the rest of the simulations carried out for this work, only thiolates (SM_e and SBu) and no more thiols (HSM_e) have been used.

3.2. Overview of the simulations

To solve the problem discussed above, the central idea is to start from a configuration where the S head groups are already in contact with the gold atoms on the nanocrystal surface. However, it is very important to assure that the final properties do not depend on the initial configuration chosen. The interaction between the S and Au atoms are actually so strong that a mutual diffusion of the ligand is markedly restricted. This limits an equilibration of the system and a dependence of the final results on the initial conditions becomes possible. Therefore we decided to start from four different initial structures: the SAM, EDGE, RANDOM and ZIGZAG configurations, which had been introduced and discussed in section 2.3.

To study the influence of the nanocrystal size and ligands, simulations were carried out for five different nanocrystal diameters (2, 4, 6, 8 and 10 nm) and methane and butane thiolate (denoted by SMe and SBu, respectively). Please note that the definition of the nanocrystal size and their exact diameters are given in the literature.²³ The four initial configurations structures discussed above were used for 4 nm and SMe. For the other conditions, only the ZIGZAG configurations were used. This is justified by the observation made in this article that the differences between the simulation results obtained for the various initial configurations are usually small. We can assume that the ZIGZAG configurations give reliable results.

To estimate a statistical error, three simulations starting from different initial configurations were performed. Since such a statistics multiplies the simulation time by a factor 3, we restricted these calculations to 2 and 4 nm, the systems with the smallest number of thiolates. As the numbers of thiolates increase with the nanocrystal size, the statistical accuracy of the simulation results is higher for nanocrystals larger than 4 nm. Therefore, the statistical errors already quite small for 4 nm can be neglected for larger nanocrystals. To study the influence of the initial configuration, a statistical error was also calculated for the SAM and ZIGZAG configurations in the case of 4 nm. The following results will show that the statistical error does not depend on the type of initial configuration.

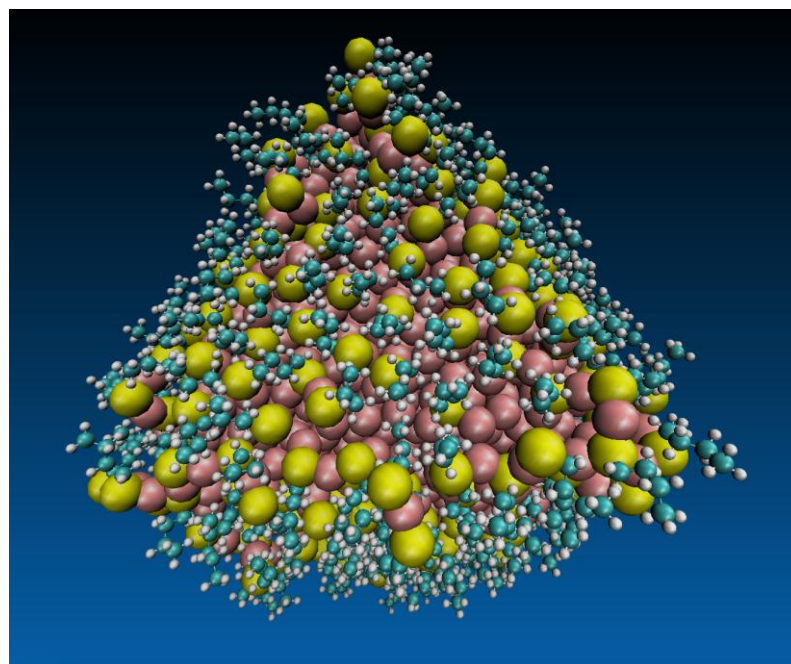
Figures 1 and 2 show the snapshots of the final structure obtained for 4 nm / SBu and 10 nm / SBu using the ZIGZAG initial configurations. In the case of 4 nm / SBu, the ligands have been removed to see the impact of the ligands on the nanocrystal structure (see Figure 1b).

The figures show that the nanocrystals are homogeneously covered with ligands. The S headgroups are in contact with the gold atoms on the surface. Due to the strong interaction with the ligands many gold atoms form adatoms letting vacancies (see Figure 1b). It can be explained by the formation of MeS-Au-SMe staples. Thus, gold atoms on the nanocrystal

surface are extracted by two S atoms close to each other to form MeS-Au-SMe staples. The formation of these staples has been widely shown by experiments and theory.⁵⁻⁸ It shows that this process markedly changes the nanocrystal morphology. It should be emphasized that previous simulations¹⁸⁻²³ were unable to correctly describe this process, since either the motion of gold atoms was restricted or the bonds between gold-gold atoms were too strong with respect to the S-Au bond. This is the fundamental new insight obtained here by the simulations using ReaxFF.

The number of ligands are all different and therefore, it is difficult to compare these systems with respect to the energy. Only the number of ligands for the RANDOM and ZIGZAG are the same, and we can compare their energies. For both configuration the same energy is obtained (-321.105 kcal/mol) which shows that both configurations cannot be distinguished by their energies.

a



b

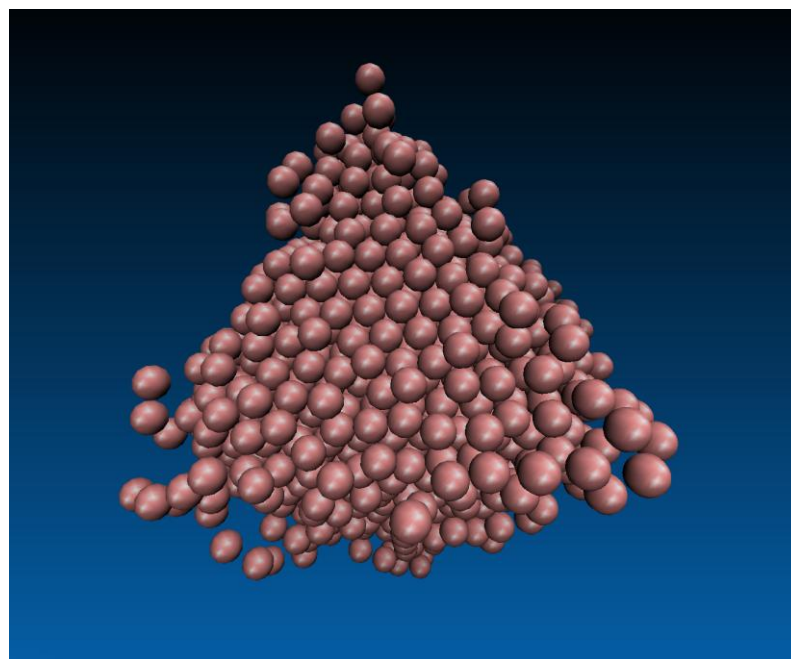


Figure 1. Snapshot of the final configuration starting from a ZIGZAG configuration of the ligands (nanocrystal diameter: 4 nm, ligand: butane thiolate). Figure b shows the same configuration as Figure a, but the ligands were removed.

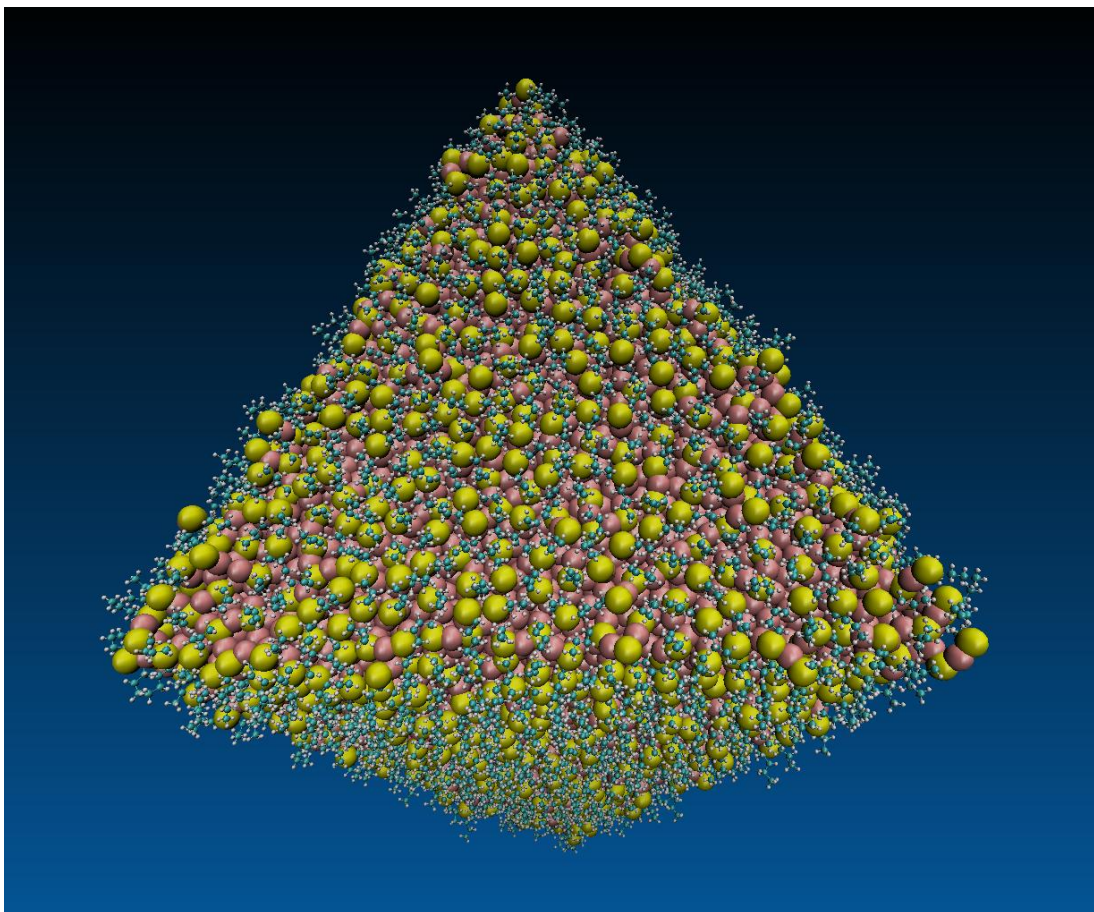
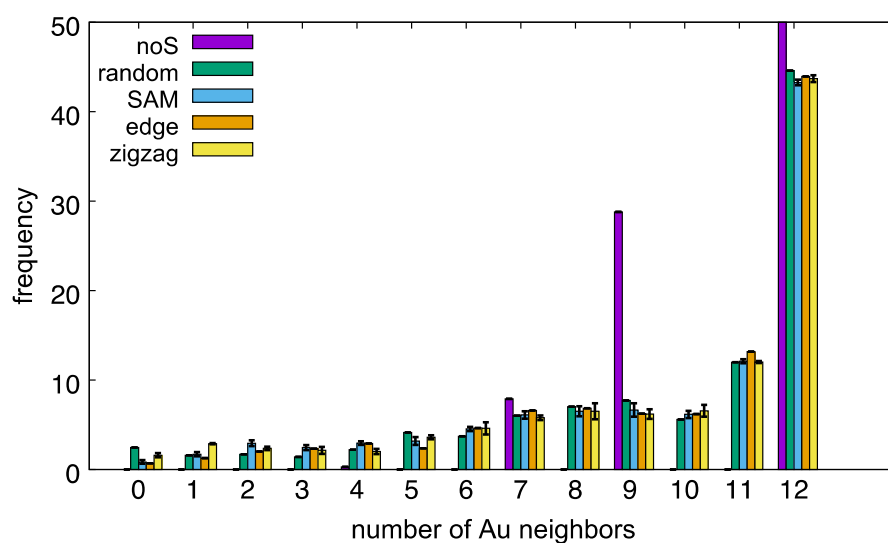


Figure 2. Snapshot of the final configuration starting from a ZIGZAG configuration of the ligands (nanocrystal diameter: 10 nm, ligand: butane thiolate).

3.3. Morphology of the gold nanocrystals

To study the change in morphology of the gold nanocrystals we first focus on the evolution of the number of neighbors for the gold atoms. For the perfect octahedral nanocrystal, the gold atoms may have four different positions: the center, facet, edge and vertex positions with 12, 9, 7 and 4 neighbors, respectively. As gold atoms move, we can expect that the frequency of the number of neighbors evolve. The frequencies of the neighbors were determined averaging the last 30 000 configurations. Two gold atoms are defined as neighbors when they are closer than $1.3 \times d_{\text{AuAu}}$, where d_{AuAu} is 2.87 Å, the average separation observed in fcc gold. To locate the atoms on the center, facet, edge and vertex positions, we use their number of neighbors in the initial perfect octahedron before the simulation. Even when the gold atoms move during the simulation, we have checked that they still stay close to these initial positions and can be associated to them. This enables us to see how the number of neighbors evolve in function of their location on the nanocrystal.

a



b

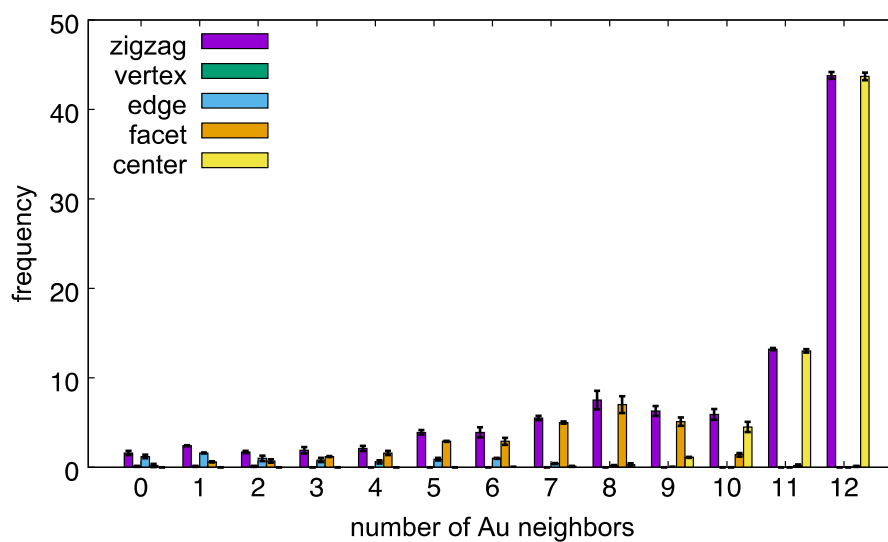


Figure 3. Frequencies of the gold atoms in contact with a given number of gold atoms (nanocrystal diameter: 4 nm, ligand: methane thiolate). a) The results are given for different initial configurations. ("noS" corresponds to the results for a perfect octahedral crystal.) b) The frequencies for the ZIGZAG configuration are distinguished if the gold atom is on the vertex, edge, facet or center positions.

Figure 3a shows the frequencies of the number of neighbors for gold for the four different initial configurations compared to the results obtained for a perfect octahedra of the same size (denoted as "noS"). The last values for the perfect octahedra correspond to those obtained by previous simulations, where the gold atoms did not move.²³ The NC diameter is 4 nm and the ligand is methane thiolate.

First, the four initial configurations give very close results. The differences observed are close to the statistical accuracy (shown for the ZIGZAG and SAM configurations). That implies that we can trust these results.

Second, the comparison of the frequencies shows that the number of neighbors markedly decreases due to the adsorption of the thiolates compared to previous simulations.²³ In particular about 2% of the gold atoms have no gold atom as neighbor, that means that they are only attached to the nanocrystals by Au-SMe-Au bonds.

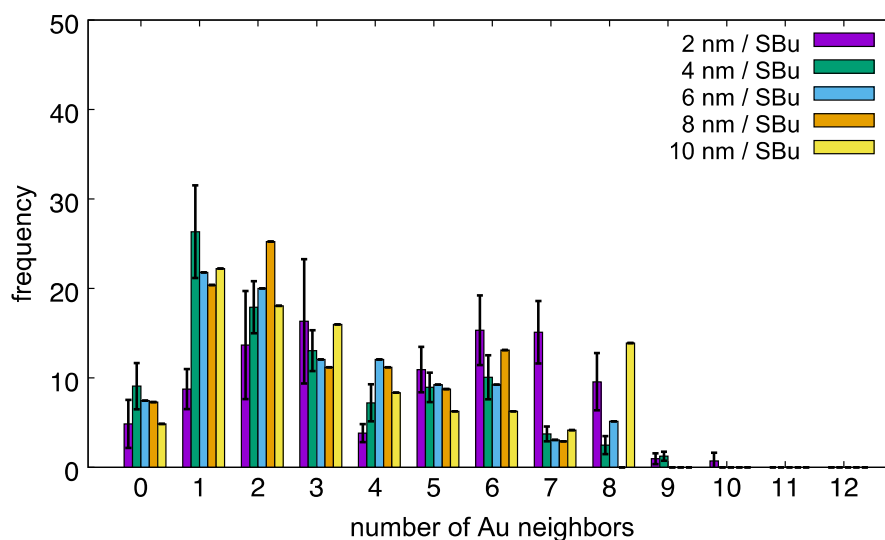
In order to better understand this result, figure 3b shows the frequency as a function of the gold atom position. We can see that many gold atoms in the center loses one or two neighbors due to the formation of staples. The gold atoms having between 3 and 9 neighbors are mainly located on the facets. Finally, the atoms without gold neighbors are mainly located on the nanocrystal edge. Actually this happens to about 10 % of the atoms on the edge. Also the atoms on the vertices are completely separated from the other gold atoms. When octahedral nanocrystals are investigated by HRTEM experimentalists observe that the vertices and edges are not atomically sharp.³⁷ This can be explained by the fact that the atoms leave their initial position as observed in our simulations. Please note that in a recent ReaxFF study of peptides on gold nanoparticles individual gold atoms also separate from the nanoparticle surface due to the formation of S-Au bonds.³⁸

We now study the influence of the ligand and the nanocrystal diameter. Figure S2 in the SI shows that the frequencies of the number of neighbors obtained for butane and methane thiolate are very similar.

In order to study the influence of the nanocrystals size, Figure 4 plots the neighbor frequencies of the gold atoms for nanocrystals diameters from 2 to 10 nm for butane thiolate. To better understand the evolution of the frequencies on the edges and facets, they were divided by the number of atoms on these positions. For nanocrystals larger than 4 nm, the frequencies do not change with nanocrystal size within the statistical accuracy. For a

nanocrystal diameter of 2 nm, the frequencies of gold atoms with no or only one neighbor markedly decreases on the edges, while they increase in the facets. Moreover on the facets the frequencies of gold atoms with more than 6 neighbors is reduced. This indicates a stronger extraction of gold atoms compared to larger nanocrystals.

a



b

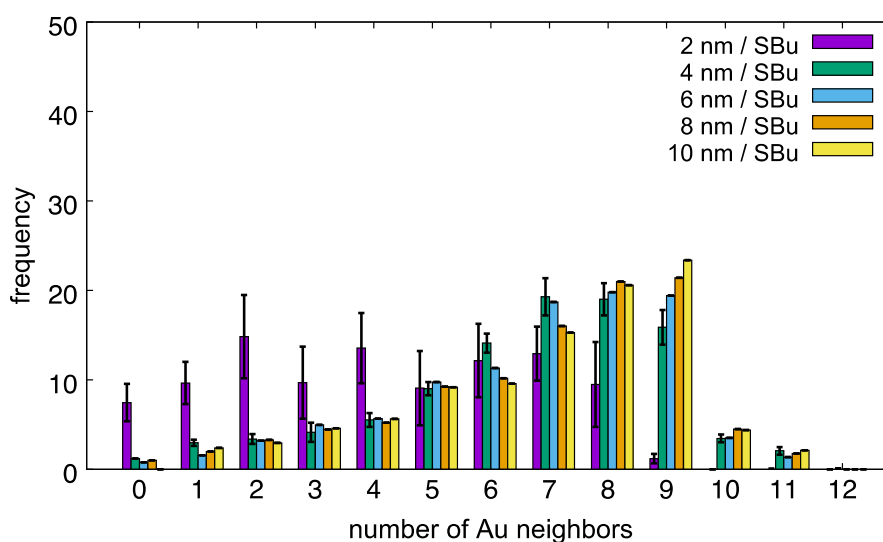


Figure 4. Frequencies of the gold atoms in contact with a given number of gold atoms for various nanocrystal diameters (ligand: butane thiolate, ZIGZAG configuration). Figure a and b show the results on the edges and facets, respectively.

3.4. Adsorption sites of the ligands

Only a very small number of ligands (less than 1 %) desorb during the simulation. We now study how many and where the ligands adsorb. A ligand is attributed to the vertices or edges if it is in contact with at least one gold atom on these positions. Ligands with no contact with gold atoms on the edges or vertices are counted for the facet. As explained in the previous section the positions of the gold atoms are determined from the number of neighbors. A thiolate is considered as in contact with a gold atom when the distance between the Au and S atom is smaller than $1.1 \times d_{\text{AuS}}$, where d_{AuS} is the Au-S distance for a thiolate adsorbed on a flat Au(111) surface (2.4 Å).

We first study how many ligands adsorb on the nanocrystal surface for a size of 4 nm.

For the RANDOM, SAM, EDGE and ZIGZAG 348, 274, 266, and 344 thiolates are adsorbed, respectively (see tables in SI). The value obtained for the ZIGZAG configuration is close to the one obtained in previous simulations (345 thiolates).²³ This is not surprising since the ZIGZAG configuration is taken from these simulations as explained in the method section and the thiolates do not desorb during the ReaxFF simulation. As discussed in articles 22 and 23 the ZIGZAG configuration gives a surface occupation of the nanoparticles in very good agreement with experimental results obtained by mass spectrometry and thermogravimetry. Obviously, the SAM and EDGE are not able to correctly reproduce the increase of surface coverage usually observed for gold nanocrystals.

We now turn to the question how many ligands adsorb on the vertices, edges and facets.

Figure 5a shows that the relative frequencies of methane thiolates for the different initial configurations are quite close. *In the SI we explain that the differences are related to the initial configurations.*

Figure 5b shows the occupation frequencies for the three positions as a function of the nanocrystals size and ligand. When the alkane chain of the ligand is increased from methane to butane, the occupation frequency on the facets decreases slightly by 3 % in average. This may be explained by steric hinderance, which is more important on the flat facets compared to the edges.

Figure 5b also shows that the occupation frequencies of vertices and edges decrease with increasing NC size. This is simply due to the fact that the place available on the facets increases more rapidly (with d_{nm}^2) compared to the edges (with d_{nm}) or vertices (constant). In the literature,²² it was shown that the number of adsorbed thiolates can be calculated from a constant surface per thiolate on the edges and facets. The same formula applies also here.

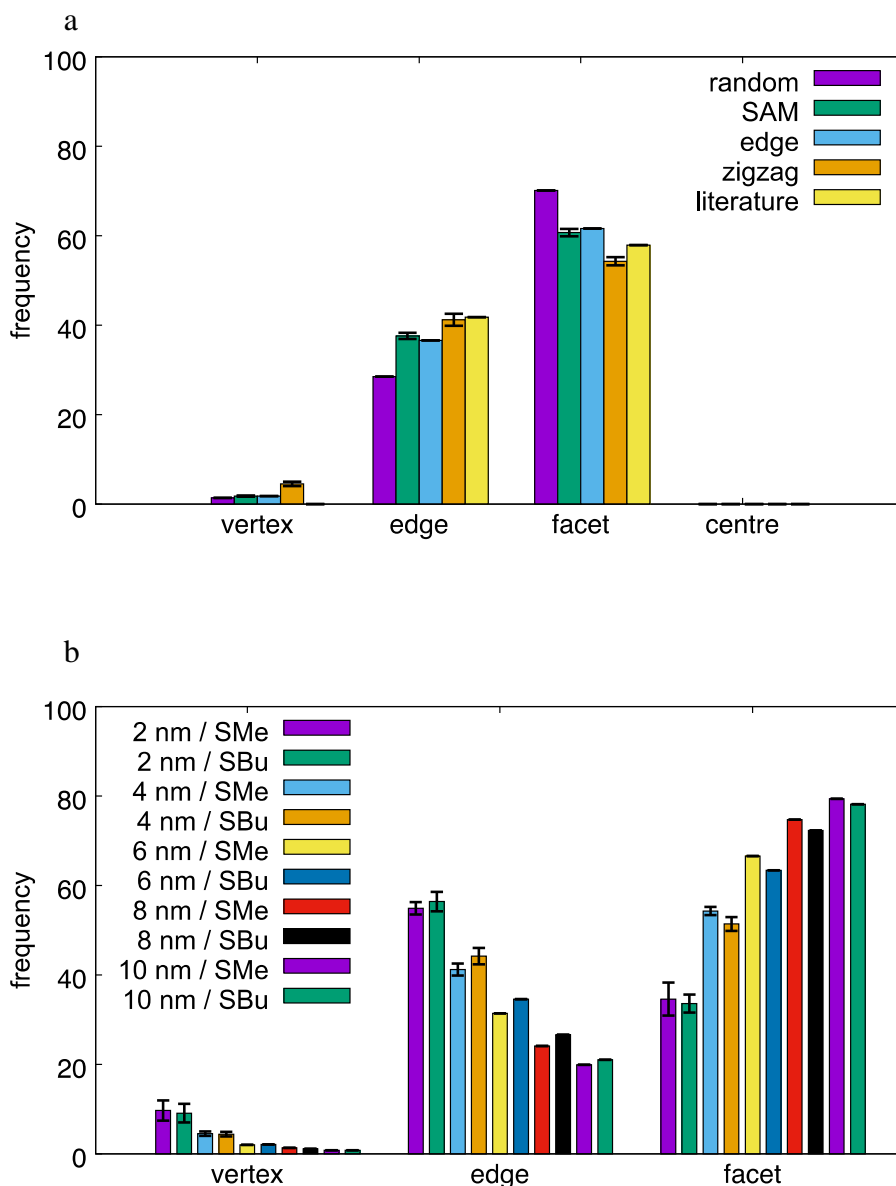


Figure 5. Relative frequencies of the S head groups as a function of their position. (a) The results are given for different initial configurations (nanocrystal diameter: 4 nm, ligand: methane thiolate). (b) The frequencies are compared for the different nanocrystal diameters and ligands.

We now study how the thiolates adsorb, in particular with how many gold atoms they are in contact. For metallic surfaces made of atoms which do not move, the number of gold atoms in contact with the ligand head group can be used to see which kind of adsorption site is occupied. Thus, one, two or three surface atoms in contact with the head group correspond to a top, bridge or hollow site, respectively. However, here the gold atoms move and we have to

be very prudent with this attribution. The case of one surface atom in contact corresponds to a top site. However for more gold atoms in contact, the adsorption site may not be clearly defined, since the gold atoms may not belong to the same atomic layer.

Figure 6 shows the frequencies of the S atoms in contact with a given number of gold atoms. In Figure 6a and b the results on the edges and facets are shown, respectively. Significant differences are observed for the different initial configurations. On the edges (Figure 6a), the largest frequency depends on the initial configuration: for the RANDOM, SAM (EDGE) and ZIGZAG configurations it corresponds to one, two and three gold atoms, respectively. We only can conclude that S atoms may be in contact with one to four gold atoms with frequencies between 20 and 50 %. The possibility of a contact with four gold atoms is impossible on a flat Au(111) surface. It is enabled here due to an additional contacts with gold adatoms which have left the initial surface.

On the facets (Figure 6b), starting from a RANDOM or ZIGZAG configuration leads to a large frequency of more than 60% for S atoms only in contact with one gold atom. This is in contrast to the results from the SAM and EDGE configurations which predict similar frequencies close to 30 % for S atoms in contact with one, two or three gold atoms. The detailed discussions in the Supporting Information show that these differences are due to the specific initial configurations. Thus, for the SAM and EDGE configurations the initial configuration with the S atoms only in bridge positions leads to an artificial bias of the structures. We can conclude that the predominant top position found by RANDOM and ZIGZAG is probably the correct structure. Actually, DFT calculations and experiments^{8,36,39,40} show that S atoms preferentially occupy top positions on Au(111) facets with a contact to one gold atoms. These results can be explained by our simulations starting from the ZIGZAG configuration.

Figure S5 plots the frequencies of the S atoms as a function of the gold atom number for various nanocrystal sizes and ligands. Except for 2 nm the differences are small and are discussed in the Supporting Information.

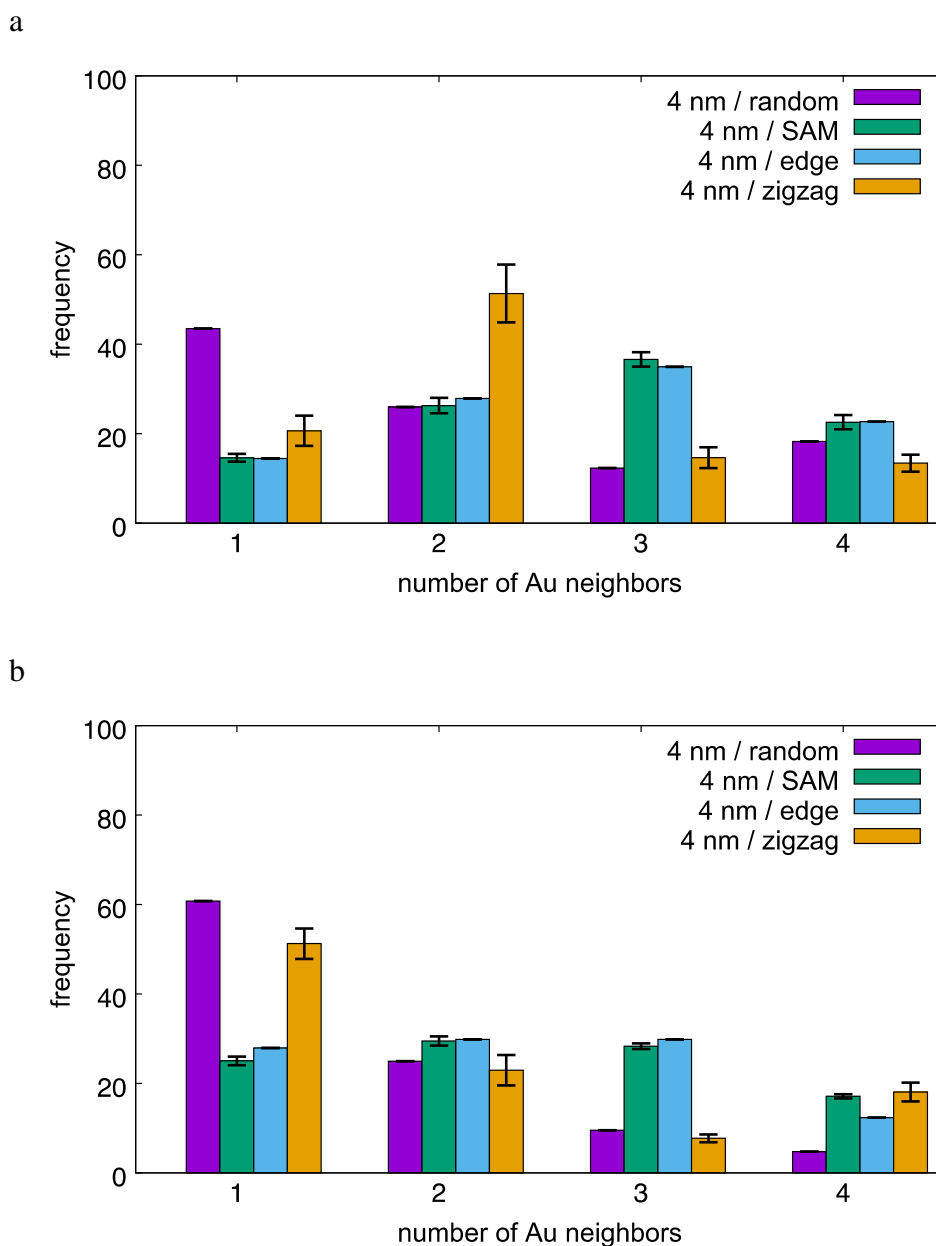


Figure 6. Frequencies of the S atoms in contact with a given number of gold atoms (nanocrystal diameter: 4 nm, ligand: methane thiolate). The results are given for different initial configurations. The frequencies are shown for the edges (a) and facets (b).

3.5. Analysis of the staple formation

As it can be seen in the snapshots of Figure 1, the formation of MeS-Au-SMe staples is observed. In the following, these staples are studied in detail. A staple is defined here by two S atoms in contact with the same gold atom (distance between the Au and S atoms smaller than $1.1 \times d_{\text{AuS}}$, where $d_{\text{AuS}} = 2.4 \text{ \AA}$, as discussed in section 3.4). Moreover the angle S-Au-S must be between 135° and 180° . This condition is necessary to exclude two S atoms in contact with the same Au atom on an Au(111) facet. To distinguish the results, a staple is considered as edge or facet if the common gold atoms belongs to the edges or facets, respectively. Figure 7 shows the staple frequencies on the edges or facets defined by the number of staples divided by the number of thiulates times 100%. This definition allows an easy comparison with experimental data.

In Figure 7a, the staple frequencies of a nanocrystal size of 4 nm and methane thiolate is shown obtained from the various initial configurations. All configurations give similar total frequencies of around 47 % except of the RANDOM one with 38 %. This difference is caused by the facets where due to the initial RANDOM position less staples are formed. For the other three configurations, similar frequencies of 67 % and 26% are obtained on the edges and facets. Compared to the facets, much more staples are formed on the edges. Actually taking into account that a staple is made of two S atoms a frequency larger than 50 % on the edges implies that in average a thiolate participates in a staple. Of course, some thiulates form more staples, while other ones not at all.

Figure 7b shows the staple frequencies obtained for the various nanocrystal diameters and the two thiulates studied here. Within the accuracy of the method, the staple frequencies do not evolve with the nanocrystal size for diameters larger than 6 nm. The ligand has also a small influence, thus the staple frequency on the facets seems to be smaller for butane thiolate. For a nanocrystal diameter of 2 nm, the staple frequencies on the edges is markedly reduced to 42 % on the edges.

The staple frequency observed for large nanocrystals on the facets (between 33 and 40 %) can be compared to experimental data. In STM studies for methane and hexane thiulates on Au(111),^{8,39} a staple frequency around 50 % is observed. However, in a more recent study combining X-ray diffraction, STM and DFT,⁴⁰ a staple frequency of 33 % was measured. Our results are in good agreement with these experiments.

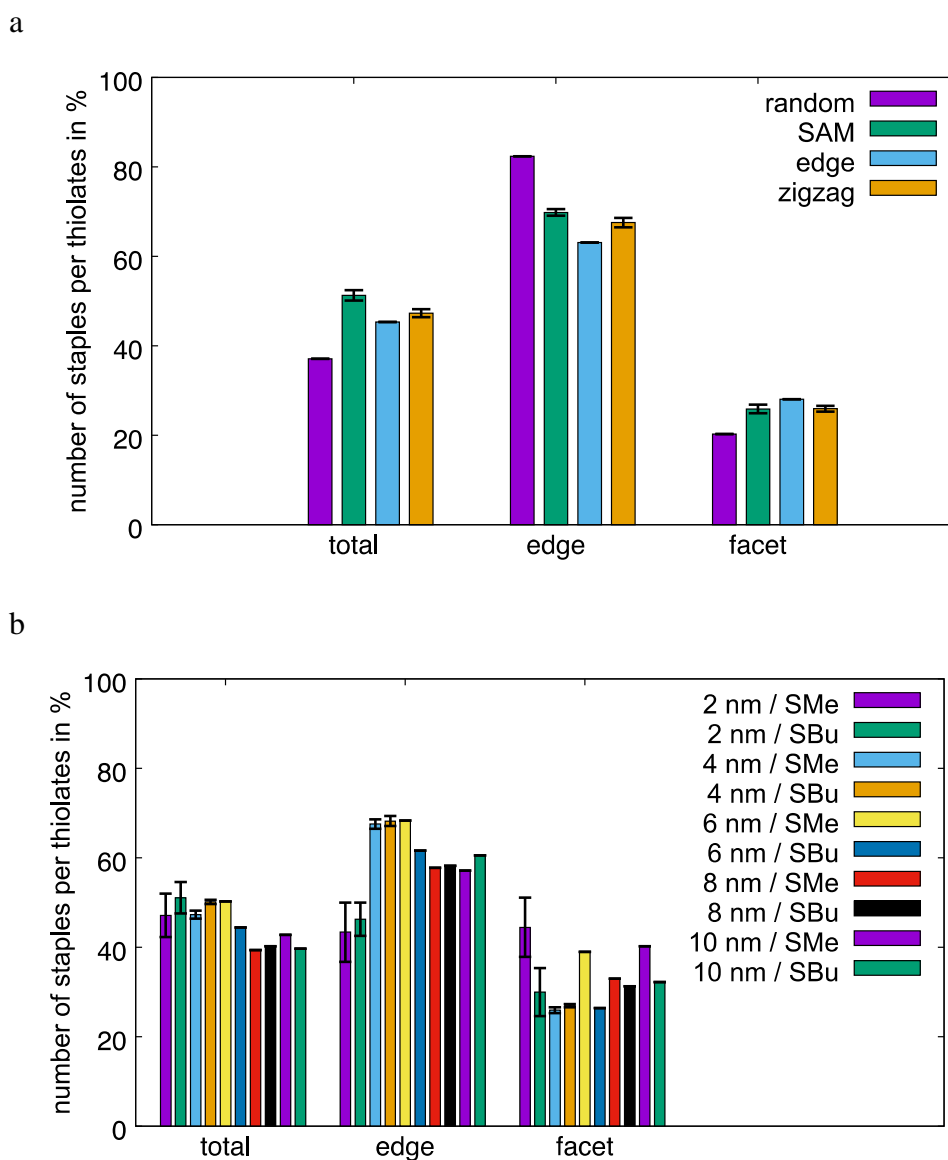


Figure 7. Number of staples per thiolates in %. (a) For a nanocrystal diameter of 4 nm and methane thiolate for the different initial configurations. (b) The results are given for different nanocrystal diameters and ligands for the zigzag configuration. The values on the edges and facets are also shown.

3.6. Average distance of the ligands and surface coverage

We finally study the average distance of neighboring S head groups of the ligands. This average distance is very interesting since it may indicate different SAMs on edges and facets.

In the classical hexagonal SAM of thiolates on gold this distance corresponds to 5 \AA . Two S atoms are considered in the following as neighboring when their distance is smaller than $1.1 \times 5 \text{ \AA}$. Figure S6 in the SI compares the average distance between neighboring S atoms for the various initial configurations. The discussion in the Supporting information show that the observed differences is simply related to a different number of adsorbed thiolates. Figure 8 plots the average S-S distances for various nanocrystal sizes and the two ligands only for the ZIGZAG configuration. The distances are also distinguished for the S atoms located on the vertices, edges and facets.

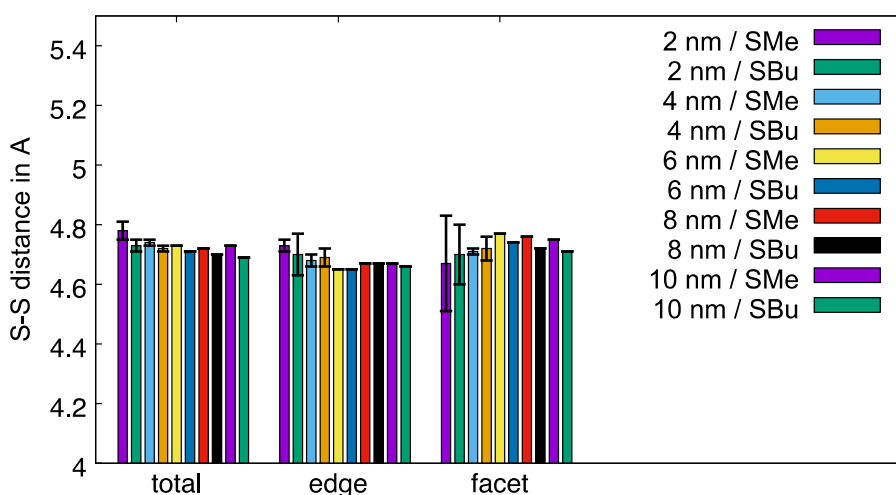


Figure 8. Average distances between neighboring S head groups. The results are given for different nanocrystal diameters and ligands. The values on the vertices, edges and facets are also shown.

Figure 8 shows that the average S-S distances are constant within the accuracy of our method for various nanocrystal sizes and the two ligands studied here. It is remarkably that the average distance does not change between the edges and facets. In previous simulations using non-reactive force fields^{22,23} it was observed that this S-S distance is reduced by about 0.2 \AA on the edges. This change was due to the formation of a new organization of the ligands

on the edges called the zigzag assembly. It explained why the surface of nanoparticles can adsorb more thiolate compared to flat gold surfaces. Here we show that reactive force fields cannot confirm such an assembly, since no change in the average distance is observed between the edges and facets. This is related to the formation of staples which have the same distance between S atoms of 4.7 Å. The staple formation actually prevents the zigzag assembly.

This leads to a new explanation why the surface of nanoparticles can adsorb more thiols. Actually we observe in the ReaxFF simulations the same large number of thiols adsorbed as in the previous ones. It is due to a higher occupation of the edges as before. But here this higher occupation is enabled by a displacement of the gold atoms which allows a larger distance between the ligands. This makes it possible that more ligands may adsorb to the edges.

Conclusions

The simulations with reactive force fields show the great importance of staple formation for gold nanocrystals.

The staple formation first leads to a marked decrease of the number of bonds between the gold atoms. Thus, about 10% of the gold atoms on the edges are only connected by a Au-S-Au bond to the nanocrystals. The simulations also show that the higher surface occupation of nanoparticles is mainly due to the edges. However, this is not due to a new organization of the ligands as proposed in the literature,^{22,23} but due to the formation of staples and the displacement of gold atoms. This appears in the observation that the S-S distance is not reduced on the edges with respect to the facets as in the previous non-reactive simulations. The staple frequencies and the predominant occupation of the top position on the facets are in agreement with experimental data.

We have shown that the ReaxFF simulations of thiolate coated nanocrystals can give reliable results with a very small dependence on the initial configurations.

Usually the influence of the nanocrystal size and alkane length of thiolate on the results is small. Only for the smallest nanocrystal of 2 nm, we observe important differences. Thus, on the edges less atoms form staples and the number of extracted gold atoms decreases, while it increases on the facets.

Finally, we have to note that no regularly ordered organizations for example of the hexagonal type is observed on the facets. This is in contrast to the previous simulations. Maybe the formation of such ordered structures would take much more time non accessible in our simulations. This remains an open question of this study, which should be addressed to in future studies.

Supporting Information

This information is available free of charge via the Internet at <http://pubs.acs.org>

Figure S1, snapshot of the final configuration starting from a total random initial configuration; Figure S2 and S3, frequencies of the gold atoms in contact with a given number of gold atoms for various ligands and nanocrystal diameters; Figure S4, snapshots after 6000 steps starting from two different initial configurations; Figure S5, frequencies of the S atoms in contact with a given number of gold atoms for different nanocrystal diameters and ligands; Figure S6, average distances between neighboring S head groups for different initial configurations. FILE "artncreaxSIfig.pdf" (PDF)

Tables S1–S2, Frequencies of gold atoms with a given number of gold neighbors for methane and butane thiolate; Tables S3–S5, Relative frequencies of the S head groups as a function of their adsorption position; Tables S5–S6, Frequencies of the S atoms in contact with a given number of gold atoms; Tables S7–S8, Frequencies of staples; Tables S9–S10, Average distances between neighboring S head groups. FILE "artncreaxSItab.pdf" (PDF)

Sections to discuss several details of the paper. FILE "artncreaxSItext.pdf" (PDF)

Program for setup of nanocrystal simulations. FILE "ntm_setup010521.py" (TXT)

Program for analysis of nanocrystal simulations. FILE "ntm_ana010521.py" (TXT)

Short Manual for the both programs. FILE manual ntm_setup ntm_ana (PDF)

Files to test the programs. FILES "nc4Me.xyz", "nc4octa.xyz", "nc4zigref.xyz", "groe1.cSAM" (TXT)

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Notes

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References

1. Daniel, M. C.; Astruc, D. Gold nanoparticles: assembly, supramolecular chemistry, quantum-size-related properties, and applications toward biology, catalysis, and nanotechnology. *Chem. Rev.* **2005**, 104, 293-346.
2. Sperling, R. A.; Rivera Gil, P.; Zhang, F.; Zanella, M.; Parak, W. J. Biological applications of gold nanoparticles, *Chem. Soc. Rev.* **2008**, 37, 1896-1908.
3. Saha, K.; Agasti, S. S.; Kim, Chaekyu, L. X.; Rotello, V. M., Gold Nanoparticles in Chemical and Biological Sensing, *Chem. Rev.* **2012**, 112, 5, 2739–2779
4. Woodruff, D. P. The interface structure of n-alkylthiolate self-assembled monolayers on coinage metal surfaces. *Phys. Chem. Chem. Phys.* **2008**, 10, 7211-7221.
5. Häkkinen H. The gold-sulfur interface at the nanoscale. *Nat. Chem.* 2012, 4, 443-455.
6. Maksymovych, P.; Sorescu, D. C.; Yates, J. T. Jr. Gold-atom-mediated bonding in self-assembled short-chain alkanethiolate species on the Au(111) surface. *Phys. Rev. Lett.* **2006**, 97, 146103.
7. Jadzinsky, P. D.; Calero, G.; Ackerson, C. J.; Bushnell, D. A.; Kornberg, R. D. Structure of a thiol monolayer-protected gold nanoparticle at 1.1 Å resolution. *Science* **2007**, 318, 430-433.
8. Cossaro, A.; Mazzarello, R.; Rousseau, R.; Casalis, L.; Verdini, A.; Kohlmeier, A.; ... Scoles, G. X-ray diffraction and computation yield the structure of alkanethiols on gold (111). *Science* **2008**, 321, 943-946.
9. Mäkinen, V.; Koskinen, P.; Häkkinen, H. Modeling thiolate-protected gold clusters with density-functional tight-binding. *Eur. Phys. J. D* **201**, 67, 38.
10. Fihey, A.; Hettich, C.; Touzeau, J.; Maurel, F.; Perrier, A.; Köhler, C.; ... Frauenheim, T. SCC- DFTB parameters for simulating hybrid gold- thiolates compounds. *J. Comp. Chem.* **2015**, 36, 2075-2087.

11. Tarrat, N.; Rapacioli, M.; Cuny, J.; Morillo, J.; Heully, J. L.; Spiegelman, F. Global optimization of neutral and charged 20-and 55-atom silver and gold clusters at the DFTB level. *Comp. Theor. Chem.* **2017**, 1107, 102-114.
12. Monti, S.; Carravetta, V.; Ågren, H. Simulation of gold functionalization with cysteine by reactive molecular dynamics. *J. Phys. Chem. Lett.* 2016, 7, 272-276.
13. Dulong, C.; Madebene, B.; Monti, S.; Richardi, J. Optimization of a New Reactive Force Field for Silver-Based Materials. *J. Chem. Theory Comput.* 2020, 16, 7089–7099.
14. Badia, A.; Singh, S.; Demers, L.; Cuccia, L.; Brown, G. R.; Lennox, R. B. Self-Assembled Monolayers on Gold Nanoparticles. *Chem.Eur. J.* 1996, 2, 359–363.
15. Badia, A.; Cuccia, L.; Demers, L.; Morin, F.; Lennox, R. B. Structure and Dynamics in Alkanethiolate Monolayers Self-Assembled on Gold Nanoparticles: A DSC, FT-IR, and Deuterium NMR Study. *J. Am. Chem. Soc.* 1997, 119, 2682–2692.
16. Hostetler, M. J.; Stokes, J. J.; Murray, R. W. Infrared Spectroscopy of Three-Dimensional Self-Assembled Monolayers: N- Alkanethiolate Monolayers on Gold Cluster Compounds. *Langmuir* 1996, 12, 3604–3612.
17. Hostetler, M. J.; Wingate, J. E.; Zhong, C.-J.; Harris, J. E.; Vachet, R. W.; Clark, M. R.; Londono, J. D.; Green, S. J.; Stokes, J. J.; Wignall, G. D.; et al. Alkanethiolate Gold Cluster Molecules with Core Diameters from 1.5 to 5.2 Nm: Core and Monolayer Properties as a Function of Core Size. *Langmuir* 1998, 14, 17–30.
18. Luedtke, W. D.; Landman, U. Structure and thermodynamics of self-assembled monolayers on gold nanocrystallites. *J. Phys. Chem. B* **1998**, 102, 6566-6572.
19. Rapino, S.; Zerbetto, F. Dynamics of thiolate chains on a gold nanoparticles. *Small* **2007**, 3, 386-388.
20. Pool, R.; Schapotschnikow, P.; Vlught, T. J. Solvent effects in the adsorption of alkyl thiols on gold structures: A molecular simulation study. *J. Phys. Chem.C* **2007**, 111, 10201-10212.
21. Lane, J. M. D.; Grest, G. S. Spontaneous asymmetry of coated spherical nanoparticles in solution and at liquid-vapor interfaces. *Phys. Rev. Lett.* **2010**, 104, 235501.
22. Djebaili, T.; Richardi, J.; Abel, S.; Marchi, M. Atomistic simulations of the surface coverage of large gold nanocrystals *J. Phys. Chem.C* **2013**, 117, 17791-17800.
23. Djebaili, T.; Richardi, J.; Abel, S.; Marchi, M. Atomistic Simulations of Self-Assembled Monolayers on Octahedral and Cubic Gold Nanocrystals. *J. Phys. Chem. C* 2015, 119, 21146–21154.

24. Järvi, T. T.; Kuronen, A.; Hakala, M.; Nordlund, K.; Van Duin, A. C. T.; Goddard, W. A.; Jacob, T. Development of a ReaxFF description for gold. *Eur. Phys. J. B* **2008**, 66, 75-79.
25. Keith, J. A.; Fantauzzi, D.; Jacob, T.; Van Duin, A. C. Reactive forcefield for simulating gold surfaces and nanoparticles. *Phys. Rev. B* **2010**, 81, 235404.
26. Järvi, T. T.; Van Duin, A. C.; Nordlund, K.; Goddard III, W. A. Development of interatomic reaxff potentials for Au–S–C–H systems. *J. Phys. Chem. A* **2011**, 115, 10315-10322.
27. Bae, G. T.; Aikens, C. M. Improved ReaxFF Force Field Parameters for Au–S–C–H Systems. *J. Phys. Chem. A* **2013**, 117, 10438-10446.
28. Monti, S.; Carravetta, V.; Ågren, H. Simulation of gold functionalization with cysteine by reactive molecular dynamics. *J. Phys. Chem. Lett.* **2016**, 7, 272-276.
29. Monti, S.; Barcaro, G.; Sementa, L.; Carravetta, V.; Ågren, H. Dynamics and self-assembly of bio-functionalized gold nanoparticles in solution: Reactive molecular dynamics simulations. *Nano Res.* **2018**, 11, 1757-1767.
30. Van Duin, A. C.; Dasgupta, S.; Lorant, F.; Goddard, W. A. ReaxFF: a reactive force field for hydrocarbons. *J. Phys. Chem. A* **2001**, 105, 9396-9409.
31. Chenoweth, K.; Van Duin, A. C.; Goddard, W. A. ReaxFF reactive force field for molecular dynamics simulations of hydrocarbon oxidation. *J. Phys. Chem. A* **2008**, 112, 1040-1053.
32. Mortier, W. J.; Ghosh, S. K.; Shankar, S. Electronegativity-equalization method for the calculation of atomic charges in molecules. *J. Am. Chem. Soc.* **1986**, 108, 4315-4320.
33. Janssens, G. O.; Baekelandt, B. G.; Toufar, H.; Mortier, W. J.; Schoonheydt, R. A. Comparison of cluster and infinite crystal calculations on zeolites with the electronegativity equalization method (EEM). *J. Phys. Chem.* **1995**, 99, 3251-3258.
34. Plimpton S., Fast Parallel Algorithms for Short-Range Molecular Dynamics. *J. Comp. Phys.* **1995**, 117, 1-19.
35. Aktulga, H. M.; Fogarty, J. C.; Pandit, S. A.; Grama, A. Y. Parallel reactive molecular dynamics: Numerical methods and algorithmic techniques. *Parallel Computing* **2012**, 38, 245-259.
36. Grönbeck, H.; Häkkinen, H.; Whetten, R.L. Gold-Thiolate Complexes Form a Unique $c(4 \times 2)$ Structure on Au(111). *J. Phys. Chem. C* **2008**, 112, 15940–15942.

37. N. Goubet, Nano et supracristaux d'or : sur l'influence de la nanocristallinité, phdthesis, Paris, 2017, <https://tel.archives-ouvertes.fr/tel-01492887>
38. Samieegohar, M., Sha, F., Clayborne, A. & Wei, T. ReaxFF MD Simulations of Peptide-grafted Gold Nanoparticles. *Langmuir* 35, 5029–5036 (2019).
39. Voznyy, O., Dubowski, J. J., Yates, J. T. & Maksymovych, P. The role of gold adatoms and stereochemistry in self-assembly of methylthiolate on Au(111). *J. Am. Chem. Soc.* **131**, 12989–12993 (2009).
40. Xavier Torrelles, Evangelina Pensa, Emiliano Cortés, Roberto Salvarezza, Pilar Carro, Cecilia Hernández Guerrero, Carmen Ocal, Esther Barrena and Salvador Ferrer, Solving the Long-standing Controversy of Long-Chain Alkanethiols Surface Structure on Au(111). *J. Phys. Chem. C* **2018**, 122, 3893–3902.