Nucleation and Growth of Stellated Gold Clusters: Experimental Synthesis and Theoretical Study

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An experimental and theoretical study on the structure and energetics of stellated gold clusters at several sizes is presented. Systematic molecular dynamics simulations on Kepler–Poisont classified clusters are performed based on cuboctahedral and icosahedral cores, following present and previous studies that suggest that stellated clusters grew from these seeds. For cluster sizes up to 10802 atoms, full atomicistic molecular dynamics simulations at room temperature have been carried out. Results show that stellated clusters in the bigger size regime maintain their star-like shape at room temperature, and by means of linear fitting of energy data to proper function models, it is predicted that the two types of stellated structures might coexist at room temperature for relatively large sizes, these findings being in good agreement with experimental results.

1. Introduction

Nowadays, one of the leitmotivs in fundamental and applied nanotechnology research is the study of stellated gold nanoparticles. From a fundamental point of view, we pursue the hypothesis that stellation on clusters (Kepler–Poisont solids) is a process that follows after the nucleation of well-defined structures, such as octahedra and icosahedra (platonic shapes) and cuboctahedra and truncated octahedra (archimedean solids).

This idea is supported in many cases by seed growth syntheses of anisotropic noble metal NPs where each one of these shape classifications could be located in size regions, although with boundaries which are not well-defined for cluster growth.

From an applied point of view, in the nanoparticle research fields there are well-established facts that drive applications research, i.e., the properties of the systems are influenced by the NP size, but it also known now that the shape strongly influences the physical and chemical properties of the NPs.

Thus, the challenge to understand how shape and size of metallic NPs relate to each other, and how these factors influence the properties of the systems under study, becomes more complex but certainly more fascinating, too. Because of their facile synthesis, their enhanced absorption and scattering cross-sections that Au and Ag NPs show under electromagnetic radiation, and their potential nontoxicity, noncytotoxicity, and good biocompatibility, they are widely studied for biological imaging and biomedical applications (cancer cell imaging and destruction, photothermal therapy, etc.). In particular, Au NPs generate heat under electromagnetic radiation, this heating effect being strong when the energy of the incident radiation is close to the plasmon frequency of the metallic NPs.

Among factors that have contributed to the comprehension and development of the energetics, thermodynamics, and kinetics of atomic and molecular clusters, we can mention the interplay between spectroscopy and theoretical techniques based on solid-state physics or other potentials supported by density-functional theory (DFT). The development of geometric models based on platonic solids, or on the most probable structures in experiments generated with quenching molecular dynamics simulations or genetic algorithms, have been proven to be essential in the development on the energetics, thermodynamics, and kinetics of atomic and molecular clusters.

Thus, suitable geometrical and potential models are available to study a small and large number of particle assemblies through nonquantum methodologies such as Monte Carlo or molecular dynamics simulations with high levels of confidence.

Under this theoretical framework, extensive studies on metallic clusters have been carried out. For instance, by using the excess energy per number of surface atoms on clusters as a diagnostic tool, Balletto et al. reported that gold clusters prefer fcc structures at sizes larger than 600 atoms and found strong competition between Dhab and fcc symmetries around N = 400 atoms. Two potential models based on DFT and SSP theories were used in those calculations, and they also found agreement with other results obtained at different levels of calculation.
Several potential models for transition and noble metals, based on the tight-binding second-moment approximation (TBSMA),\textsuperscript{16,17} have been proposed. The parametrization by Rosato et al.,\textsuperscript{18} (RGL model) and a second parametrization of the RGL by Cleri and Rosato\textsuperscript{19} (CR) are examples.\textsuperscript{25,26} All these kinds of models include the repulsive pairwise Born–Mayer potential to stabilize the system. One of the main characteristics of those models is the inclusion of many body effects ensuring correct estimation of several bulk properties, such as cohesive energies, vacancies, surface effects, etc. The correct estimation of those bulk properties, mainly cohesive energy, surface effects, and surface reconstructions, has given confidence to extend the model to atoms in a cluster environment.\textsuperscript{15} Thus, with these reliable potential models at hand, general trends can be obtained. For example, significant knowledge on the thermal behavior of gold clusters is well-known for specific geometries based on crystalline and noncrystalline motifs, such as fcc, icosahedral, and decahedral clusters.\textsuperscript{15}

In this work, by means of classical MD simulations, and the CR interatomic potential model, we study the structure and dynamics of stellated gold nanoclusters with icosahedral and cuboctahedral seeds, biased mainly by the present experimental results on gold nanoparticles and previous reports on stellated (piñata-like) clusters.\textsuperscript{2} Stellated Au nanoparticles have been synthesized at room temperature and atmospheric pressure. Figure 1 shows the great rate of production of these stellated clusters, and the high-resolution transmission electron microscopy (HRTEM) images at different orientations clearly show highly symmetric pyramidal structures with slightly smoothed apexes. Experiments have shown a high stability of the cluster shapes, i.e., they do not change in days and even months after deposition in an inert environment. These facts support the hypothesis that stellated gold particles could have cuboctahedral and icosahedral cores, but both with surface tetrahedral growth along the high symmetry axes; see Figure 2. For insight into the structural and thermal behavior of these stellated structures, mainly at room temperature, we present a systematic study of the structural and thermal behavior of two groups of gold clusters that are constructed based on those structures.

2. Experimental Details

A. Materials and Methods. Hydrogen tetrachloroaurate trihydrate (HAuCl₄·3H₂O) and ascorbic acid were purchased from Sigma-Aldrich and used as received. Multibranched polyhedral gold nanoparticles were prepared by colloidal reduction in aqueous solution at ambient conditions according to previous literature methods.\textsuperscript{2} A volume of 0.5 mL of 0.1 M HAuCl₄ aqueous solution (50 µmol) was rapidly added to an aqueous solution of ascorbic acid (2 mmol in 40 mL of H₂O) under vigorous stirring. The solution immediately changed color to opaque orange-red within 1–2 s. All the samples were purified by washing with ethanol and centrifuging and were finally dispersed in ethanol.

B. TEM Characterization. The Au nanostar samples were characterized with an ultrahigh resolution scanning electron microscope (SEM) FEG Hitachi S-5500 (0.4 nm at 30 kV) with a BF/DF Duo-STEM detector and a high resolution transmission electron microscope (HRTEM) Jeol JEM-2010F FE-TEM with

Figure 1. (a) Low resolution transmission electron microscopy image of gold nanoparticles with a high production rate of stellated particles. (b) A magnified region where more detail of these stellated clusters is observed.

Figure 2. Transmission electron microscopy images of gold particles with assumed (a) cuboctahedral and (b) icosahedral seeds. Models that resemble these images are shown in panels c and d. (e) SEM image shows the coexistence of both kinds of stellated clusters.
Figure 3. UV–vis absorption spectra of stellated clusters. For the resuspended stellated gold nanoparticles, a pronounced asymmetric absorbance maximum is apparent at ≈610 nm, and a lower shoulder in the spectrum is observed at ≈835 nm, which revealed that star-shaped gold nanoparticles present spectral peaks that can be assigned to transverse and longitudinal plasmon resonances of the gold nanoparticles.

an accelerating voltage of 200 kV, equipped with a Schottky-type field emission gun and a point-to-point resolution of 0.19 nm. Samples for TEM studies were prepared by directly placing the gold nanoparticles onto a holey carbon TEM grid.

C. UV–vis Absorption Spectra. Absorption spectra for the Au stellated samples were obtained with an Agilent 8453 UV–vis spectrophotometer. Samples were prepared by diluting the original reaction product with distilled water.

Figure 3 shows the UV–vis absorption spectra of resuspended stellated gold nanocrystals. The rapid growth of nucleation particles and the subsequent development of stellated clusters took place within the first few minutes of reaction. The spectrum shows two broad absorption bands centered at ≈610 nm, and a lower shoulder is observed at ≈835 nm. The band centered at 610 nm has slightly higher absorbance than the one shown at 835 nm. The spectral data obtained suggest that there are two different morphologies of the gold nanostructures formed. The peak around 610 nm represents the plasmon band of the small tips of irregular nanostructures in the solution, and the peak centered at 835 nm is associated with the elongated tip structure of the stellated clusters. These general features of the UV–vis spectrum of star-like gold particles are in general agreement with previous reports.27–30

3. Theoretical Background and Methodology

The functional form of the TBSMA for pure atomic systems, also known as the Gupta potential,16 is given by

$$V(r_i) = \sum_{j \neq i} A \exp(-p\Delta r_{ij}) - \left( \sum_{j \neq i} \xi^2 \exp(-2q\Delta r_{ij}) \right)^{1/2}$$

(1)

The first term is the repulsive Born–Mayer pairwise potential, and the second one is the tight-binding based attractive nonpairwise potential which takes into account many-body effects. $\Delta r_{ij} = (r_j - r_i)r_0$ is the fractional change in distance between atom $i$ and atom $j$, and $r_0$ is the distance between first nearest-neighbors in the bulk. The five parameters, $A$, $\xi$, $p$, $q$, and $r_0$ must be determined for each particular transition or noble metal atom by a parametrization procedure using bulk data.18,19,31 If only first nearest-neighbors are taking into account in eq 1, and if the equilibrium condition is fulfilled, then the number of parameters is decreased from five to three:

$$A = \frac{q |E_{coh}|}{p - q}$$

(2a)

$$\xi = \frac{p |E_{coh}|}{p - q \sqrt{Z}}$$

(2b)

where $E_{coh}$ is the experimental cohesive energy of bulk used in the parametrization, and $Z$ is the number of first nearest-neighbors in the crystal.

Some sets of parameters for gold (fcc crystal) are given in Table 1. In these models, values for $A$ and $\xi$ are very close to those calculated from eqs 2 using the experimental value $E_{coh} = -3.78$ eV/atom and $Z = 12$, both from gold fcc-crystal.32 At first sight, differences and similarities between these potential models can be obtained from the fractional change in total energy accompanying a fractional change in distance between first nearest-neighbors $\epsilon = (r_j - r_i)r_0$, which to a second-order approximation in $\epsilon$ is roughly given by

$$\frac{\Delta E}{|E(0)|} = \sigma_1 \epsilon^2$$

(3)

where $\Delta E = E(\epsilon) - E(0)$, $E$ is the total energy, and $\sigma_1 = pq^2/2$, see ref 25. The $\sigma_1$ values for the CR and RGL models differ 1.5% from each other, and the values among BFFMM and CP differ 0.8%, corresponding to the lower and bigger values to the CR and CP models, respectively. Thus, according to $\sigma_1$ values and eq 3, the BFFMM potential is as sticky as the CP model, and the CR model is slightly less sticky than the RGL, CP being more sticky than the CR model. However, according to the formula

$$\frac{\Delta E}{|E(0)|} = \frac{1}{p - q} \left( q(e^{p\epsilon} - 1) - p(e^{-q\epsilon} - 1) \right)$$

(4)
the four parameter sets given in Table 1 under the GROMOS96 at room temperature of the SC and SI gold clusters described
0.115, respectively. Thus, according to eq 4 the CP model is twenty tetrahedral clusters, each with
practical value for the time-step is 1 fs.35 Also under this scheme, ensured for a time-step of 2 fs, if the Shake method is applied; is the weak-ensemble,37 which has intermediate property produced by MDS applications using Berendsen’s thermostat.

δ
where no approximations for ε have been used, and the similarity between the BFFMM and CP models only occurs for displacements less than 1.5% of r0, as can be seen from the plots in Figure 4. In fact, crossovers between the CP and the BFFMM, RGL, and CR models occur at ε = 0.0085, ε = 0.093, and ε = 0.115, respectively. Thus, according to eq 4 the CP model is less sticky than the other potentials, but only for ε ≥ 0.115.

A. Simulation Details. In order to perform MD simulations at room temperature of the SC and SI gold clusters described above, the Au potential model given by eq 1 was used, applying the four parameter sets given in Table 1 under the GROMOS96 scheme.33 This package applies the leapfrog algorithm to integrate Newton’s classical equations of motion under vacuum or periodic boundary conditions.34 High numerical stability is ensured for a time-step of 2 fs, if the Shake method is applied; otherwise, it is 0.5 fs. Those time-steps values are commonly used for flexible biological molecules,33 for metallic atoms, a practical value for the time-step is 1 fs.35 Also under this scheme, the system could be weakly or strongly coupled to a temperature bath using Berendsen’s thermostat.36 The numerical ensemble produced by MDS applications using Berendsen’s thermostat is the weak-ensemble,37 which has intermediate property between the canonical (N, V, T; α = 0) and microcanonical (N, V, E; α = 1) ensembles. Here, α is a constant in equilibrium but dependent on the temperature coupling parameter.36,37 In the practice, α is determined from the ratio of standard deviations of kinetic and potential energies,

\[
α = \sqrt{\langle (\delta E_{\text{kin}})^2 \rangle / \langle (\delta E_{\text{pot}})^2 \rangle}
\]

where \( \delta E_k(t) = E_k(t) - \langle E_k \rangle \) stands for the instantaneous fluctuation of property \( z \) (kinetic or potential energy), and \( \langle \rangle \) denotes average time.

B. Geometrical Description. Because any stellated gold clusters considered in this work are made up of one icosahedral or one cuboctahedral cluster in the core, and regular tetrahedral clusters attached to their (111) faces, we will refer to them as stellated icosahedral (SI) and stellated cuboctahedral (SC) clusters, respectively. Specifically, each SC gold cluster is made up of one Mackay icosahedral cluster with \( N(n) = 10(n/3)^3 - 5n^2 + (11/3)n - 1 \) atoms, and twenty tetrahedral clusters, each with \( N_T(k) = k(k+1)(k+2)/6 \) atoms and attached to each one of the twenty (111) facets of the icosahedral cluster. In a similar way, each SC gold cluster is made up of one cuboctahedral cluster with \( N(k+1) \) atoms, and eight tetrahedral clusters, each with \( N_T(k) \) atoms and attached to each one of the eight (111) facets of the cuboctahedral cluster. Hence, the number of atoms of any SI cluster is given by \( N_{SI}(k) = N(k+1) + 20N_T(k) \), while \( N_{SC}(k) = N(k+1) + 8N_T(k) \) is the number of atoms of any SC cluster. \( N_{SI}(k) \) and \( N_{SC}(k) \) are only different in the number of tetrahedrons, and they can also be expressed as

\[
N_{SC}(k) = \frac{14}{3} k^3 + 9k^2 + \frac{19}{3} k + 1 \quad (6a)
\]

\[
N_{SI}(k) = \frac{20}{3} k^3 + 15k^2 + \frac{31}{3} k + 1 \quad (6b)
\]

with \( k \geq 1 \).

The gold clusters considered in this work are those SC clusters with \( k \leq 13 \), and those SI with \( k \leq 11 \), shown in Figure 5. In all the initial geometrical models the distance between first nearest-neighbor atoms is fixed to the first nearest-neighbor distance of bulk gold, \( r_0 = 2.88 \) Å.

4. Results and Discussion

Figure 5 displays the unrelaxed stellated clusters used in this study. To prepare these SI and SC gold clusters for MD simulations at \( T = 298 \) K, we have first slightly relaxed each one of them with the steepest-descent method using the four potential models in Table 1. Although the main purpose of the minimization procedure is to reduce the internal strain of the cluster, and the consequent reduction of computer effort at the equilibration period, we have analyzed these results to gain insight into how investigating the residual stress is reflected into the structures, how the surface and volume contributions to the total energy behave as a function of cluster size, and what type of the stellated structures is the most favorable. Similarities and differences between the results obtained using older and newer gold potential models (Table 1) are also enhanced and analyzed at this stage in order to choose the appropriate potential to perform the simulations at room temperature. Thus, a conscientious analysis of the structural and energetic results obtained under this procedure is presented in section 4A. In section 4B, we have posed similar questions for the equilibrated clusters at \( T = 298 \) K, and the results have been analyzed in the same way, but only for the CR potential model, which was elected after the analysis in section 4A.

A. Relaxed Clusters. In cluster physics it is common to describe atoms as hard spheres and to use them as a linear length unit. Following this idea, in the microcrystal size regime (where a high rate of the total \( N \) atoms belong to the bulk) the particles are \( N^{1/3} \) atoms long, with area facets proportional to \( N^{2/3} \). Only some atoms belong to the surface (\( \sim N^{2/3} \)), located predominately on the facets, and only a negligible number on the edges and the vertices. On the contrary, when the cluster size is decreased, almost all the atoms tend to be at the surface. In this case, however, the respective contribution to the surface energy that each amount of atoms in the edges, the vertices, and the facets tend to compete with each other, and the extreme case is for the very small clusters that contain only vertex atoms. Therefore, it would be helpful to obtain a function that gives insight to which range of \( N \), the macro/micro (\( N_{\text{surf}} \ll N \)) or the nano (\( N_{\text{surf}} \approx N \)) character of any studied cluster, is manifested.

For this purpose, a function is proposed for the number of surface atoms \( N_{\text{surf}} \) in terms of \( N^{1/3}, N^{2/3} \), and a constant, as follows
Clusters tend to be closer to its asymptotic value, 2. Note that some parameters are necessarily negative. The asymptotic value for a simple cubic cluster, \( \text{SC} \), and SI clusters are given in Table 1 were used, we have to facilitate discussions. In this figure, the solid and dotted lines are obtained by linear fitting of SC and SI \( N_{\text{surf}} \) data to functions of the form given by eq 7, respectively. Here the function \( N_{\text{SC}}(N) \) is for \( N \geq 21 \), while \( N_{\text{SI}}(N) \) is for \( N \geq 135 \). The coefficients of the fitting functions for the SC and SI clusters are given in Table 2. Note that some parameters are necessarily negative.

As can be seen from Figure 6, calculated values for SC clusters tend to be closer to its asymptotic value, \( \alpha_{\text{SC}} = +6.449 \), than those values for SI clusters, that tend to be \( \alpha_{\text{SI}} = +8.466 \). The asymptotic value \( \alpha_{\text{SC}} \) is greater than the asymptotic value for a simple cubic cluster, \( \alpha_{\text{cubic}} = 6.0 \), because the SC clusters are based on a truncated fcc with tetrahedral units attached to the (111) faces. The value \( \alpha_{\text{SI}} = +8.466 \) is explained by a similar reasoning. For cluster sizes of \( \Omega(10^3) \), values of the fitting functions \( N_{\text{SC}} \) and \( N_{\text{SI}} \) are around the 2.2% and 4.6% of their asymptotic values, respectively. Thus, one could expect stronger surface effects for SI clusters than for the SC clusters, or one could expect that the SC clusters already behave as macro clusters \( (N_{\text{surf}} \propto N^{2/3}) \) for relatively small sizes, \( N \sim 10^6 \), so that many properties of SC could be dominated by volume atoms. For SI clusters in the same range, one could expect properties dominated by surface atoms. As a note of caution, the stellated clusters have very specific sizes, see eqs 6, because they are constructed using complete tetrahedral units mounted on the eight triangular faces of the cuboctahedra or over the twenty faces of the icosahedral clusters. Hence, detailed interpolation or extrapolation results from eq 7 must be taken with care.

In the small size range, the stellated clusters with sizes \( N_{\text{SC}}(4) = 469 \) and \( N_{\text{SI}}(4) = 709 \) contain tetrahedral units of 20 atoms. Note that tetrahedral gold cluster with 20 atoms have been proven to be the more stable gold isomer.40 In this respect, we also note that after the slight relaxation processes, where each of the potential models displayed in Table 1 were used, we have observed that the shape of each cluster in Figure 5 is maintained; the relaxed clusters are contracted on the average, as expected for these kind of potential models,15 this result being more evident in the smaller ones due to the high value of the surface/volume ratio, but the peaks of all the clusters are maintained, which can be attributed to the same mechanism that maintains vertex atoms of the global minima tetrahedral cluster of Fernandez et al.40

In order to explore the energetic trends of the relaxed SC and SI clusters under the potential models given in Table 1, we have first fitted the potential energy data of each series to a function of the form (see ref 15 and references therein)

\[
E(N) = AN + BN^{2/3} + CN^{1/3} + D \tag{8}
\]

where the coefficient \( A \) is proportional to the energy per atom of the bulk-like atoms, that follows from the asymptotic behavior.
of \( E(N)/N \) for large clusters. The number of bulk atoms is taken proportional to the cluster size \( N \). Thus, at least for large clusters, the first term in the eq 8 could be interpreted as the contribution to total energy due to bulk atoms, and the last three terms together as the contribution to total energy due to the atoms at the surface. The explicit dependence on \( N^a(3/2, 2/3, \text{and } 0) \) comes from the splitting of the full number of surface atoms into facet atoms (proportional to \( N^{3/2} \)), edge atoms (proportional to \( N^{2/3} \)), and vertex atoms (a constant).

Therefore, by construction, the first term in eq 8 is interpreted as the total volume contribution to the energy, and the second, third, and fourth terms together are interpreted as the total surface energy contribution (see ref 15 for details). As in the case of \( N_{\text{surf}}(N) \), see eq 7, the coefficients in eq 8 must be free parameters, and high correlation among them are expected (mainly among coefficients B, C, and D) when fitting data of small, intermediate, or large size clusters to this equation.

The parameters for the fit to each type of stellated clusters and potential models are given in Table 3. To avoid large asymptotic standard errors in the linear fitting data of SI clusters, the coefficient C is excluded from its fitting process. Note that, for the potential models RGL and BFFMM, the asymptotic values for the binding energy, \( A_{\text{SC}} \), are lower than the experimental cohesive energy of bulk used in the parametrization of each of the potential models (see Table 1); however, they are very close to the experimental cohesive energy, \( E_{\text{coh}} = -3.81 \text{ eV/atom} \) reported in ref 41. For the CP model, \( A_{\text{SC}} \) is exactly the calculated value of the cohesive energy of bulk Au reported by Chamati and Papanicolaou,26 and for the CR model, the value of \( A_{\text{SC}} \) is very close to the experimental cohesive energy of bulk used in its parametrization.19

In order to explore which type of relaxed structure is more favorable, we have used as a diagnostic tool the excess energy per \( N^{2/3} \), defined by,\(^{15}\)

\[
\Delta(N) = \frac{E - NE_{\text{ref}}}{N^{2/3}} \tag{9}
\]

where \( E \) stands for the total potential energy of one cluster of size \( N \), and it is common to take for the reference energy \( E_{\text{ref}} \) the experimental cohesive energy of the bulk used in the parametrization of the potential model; see Table 1. Here, for each potential model, \( \Delta(N) \) is calculated using \( E_{\text{ref}} = A_{\text{SC}} \), where \( A_{\text{SC}} \) is given in Table 3. The results of the calculations of \( \Delta(N) \) using each of the potential models in Table 1 and the steepest-descent method are given in Figure 7. It can be observed from this figure that at this stage of the simulations, almost all SC clusters, except \( N_{\text{SC}}(1) = 21 \), are more favorable than the SI clusters. This behavior occurs for all potential models, except the CP model which also excludes \( N_{\text{SC}}(2) \). Similar results have been found by Baletto et al.,25 using the RGL and embedded-atom models, but for nonstellated icosahedral and cuboctahedral clusters. However, as can be seen from the calculated data in the figure, the effects of mounting tetrahedral motifs on the triangular faces of cuboctahedral or icosahedral clusters changes significantly the behavior of \( \Delta(N) \). For instance, \( \Delta \) data of icosahedral clusters in ref 25 is concave up, while the \( \Delta \) data of SI clusters in Figure 7 is concave down. For Lennard–Jones icosahedral and fcc cluster data,\(^{24,25}\) it has been found that \( \Delta \) is concave down for both types of clusters. We have explored the concavity effect by expressing \( \Delta(N) \) in the form

\[
\Delta(N) = aN^{1/3} + b + cN^{1/3} + dN^{2/3} \tag{10}
\]

which follows from eq 8 and eq 9. The parameter \( a = A - E_{\text{ref}} \) is interpreted as the strain or elastic energy per atom of the cluster.\(^{15,43,44}\) It is well-known that for clusters with fcc symmetry, \( a_{\text{SC}} \) is negligible because the bulk energy per atom \( A_{\text{SC}} \) is the optimum. On the contrary, it is also well-known that the noncrystallographic symmetry of the clusters frustrates the elimination of strain by the minimization process, and consequently they can accumulate that energy as elastic energy.\(^{15,43,44}\) which increases with cluster size. In principle, \( A \) must be higher or equal to the cohesive energy of the bulk crystal, \( E_{\text{coh}} \), which can be appreciated as the optimum energy per atom of volume atoms; however, in practice, when fitting MDS results to eq 8, \( A \) could be slightly lower than \( E_{\text{coh}} \). This could be attributed to the linear fitting of MDS data and/or to the cutoff radius used in the interactions: in all potential models we have included

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**TABLE 3:** The Coefficients for the Fitting Function, eq 8, for the Steepest-Descent Relaxed SC (first row) and SI (second row) Clusters with the Potential Models Given in Table 1 (units are eV/atom)

<table>
<thead>
<tr>
<th>model</th>
<th>( A )</th>
<th>( \sigma' )</th>
<th>( B )</th>
<th>( C )</th>
<th>( D )</th>
</tr>
</thead>
<tbody>
<tr>
<td>CR</td>
<td>-3.7795 ± 0.0003</td>
<td>0.0000</td>
<td>1.570 ± 0.007</td>
<td>-0.71 ± 0.06</td>
<td>1.68 ± 0.11</td>
</tr>
<tr>
<td></td>
<td>-3.7687 ± 0.0002</td>
<td>0.0108</td>
<td>1.678 ± 0.003</td>
<td>-0.73 ± 0.05</td>
<td>-3.53 ± 0.05</td>
</tr>
<tr>
<td>RGL</td>
<td>-3.8256 ± 0.0002</td>
<td>0.0000</td>
<td>1.454 ± 0.007</td>
<td>-0.73 ± 0.05</td>
<td>1.76 ± 0.10</td>
</tr>
<tr>
<td>BFFMM</td>
<td>-3.8160 ± 0.0002</td>
<td>0.0096</td>
<td>1.554 ± 0.003</td>
<td>-3.21 ± 0.04</td>
<td></td>
</tr>
<tr>
<td>CP</td>
<td>-3.8284 ± 0.0002</td>
<td>0.0000</td>
<td>1.436 ± 0.005</td>
<td>-0.77 ± 0.04</td>
<td>1.84 ± 0.08</td>
</tr>
<tr>
<td></td>
<td>-3.8186 ± 0.0002</td>
<td>0.0099</td>
<td>1.533 ± 0.004</td>
<td>-3.16 ± 0.05</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-3.7600 ± 0.0001</td>
<td>0.0000</td>
<td>2.967 ± 0.004</td>
<td>-0.54 ± 0.03</td>
<td>0.34 ± 0.06</td>
</tr>
<tr>
<td></td>
<td>-3.7336 ± 0.0013</td>
<td>0.0264</td>
<td>3.125 ± 0.021</td>
<td>-7.87 ± 0.29</td>
<td></td>
</tr>
</tbody>
</table>

\( \sigma' = A - E_{\text{ref}} \), where \( E_{\text{ref}} = A_{\text{SC}} \).
been conducted as follows: for each cluster a sample of clusters of each series \( k = 1, 2, 3 \) are structures of low-symmetry or amorphous-like clusters. The last cluster in each series corresponds to \( N_{\text{SI}}(9) = 6169 \) (bottom), and \( N_{\text{SC}}(10) = 5631 \) (top).

Figure 8. Same caption as for Figure 5, in this case for the average equilibrium configurations of the stellated gold clusters obtained by MDS at room temperature. In the first row are those gold clusters based on initial structures with a cuboctahedral core, and in the second row those with an icosahedral core. The first three clusters of each series \( k = 1, 2, 3 \) are structures of low-symmetry or amorphous-like clusters. The last cluster in each series corresponds to \( N_{\text{SI}}(9) = 6169 \) (bottom), and \( N_{\text{SC}}(10) = 5631 \) (top).

more than one coordination shell in the interactions. In any case, because one is interested in the relative stability of the two types of clusters, one can determine negative values for \( \sigma \) in eq 10, we have used for the reference energy \( E_{\text{ref}} \) the lower value for \( A \) in each potential model, instead of the experimental cohesive energy of bulk used in the parametrization of the potential model; see Table 1.

In Figure 7, the solid and dotted lines in each plot are the curves \( \Delta_{\text{SC}}(N) \) and \( \Delta_{\text{SI}}(N) \) obtained with the coefficients given in Table 3, for the potential models CR (a), CP (b), RGL (c), and BFFMM (d). Note that, in general, the asymptotic value for the binding energy \( \Delta_{\text{SC}} \) is lower than the experimental cohesive energy of bulk used in the parametrization of the potential model; see Table 1. As pointed out in the preceding paragraph, to avoid negative values of \( \sigma_{\text{SC}} \), we have used \( E_{\text{ref}} = \Delta_{\text{SC}} \) in eq 10 for the SC and SI clusters. This procedure has no effect in the present analysis, because we have only changed the reference point of energy. For all the potential models, the respective functions, \( \Delta_{\text{SC}}(N) \) and \( \Delta_{\text{SI}}(N) \), predict only one crossover size. Only the crossover sizes for the RGL, BFFMM, and CR models agree with the rule: the larger is \( pq \), the smaller are the crossover sizes. The CP model has the higher value of \( pq \), and also the higher value of the crossover size. The exact values of the crossover sizes have no real significance, because the calculations have been limited to clusters sizes given in eqs 6. We can only infer from these results that both types of clusters could coexist around these sizes. For any potential model, no other crossover sizes occur for the larger clusters of both types, because their asymptotes (straight lines in \( \Delta(N^{1/3}) \), in Figure 7) are not intersected. Thus, each one of the potential models predict only one crossover size, which occurs for relatively small cluster sizes. Therefore, at this stage of the MD simulations, we could partially conclude the following: (a) all the slightly relaxed structures maintain the star-like shape of the initial structures; (b) all SC clusters, except the smaller cluster, are more favorable than the SI clusters; (c) for SI structures, the most strained are given by the CP model while the less strained by the RGL model (elastic energy values given by the CR and BFFMM models are very close to the value given by the RGL model); and (d) only the asymptotic value for the binding energy \( \Delta_{\text{SC}} \), given by the CR model, is very close to the value of the experimental cohesive energy used in its parametrization.

B. Equilibrated Clusters at \( T = 298 \text{ K} \). MD simulations at room temperature of the relaxed clusters described above have been conducted as follows: for each cluster a sample of mechanical states of length 0.25 ns has been produced in a weak-ensemble approximating the microcanonical-ensemble \( (\alpha = 1) \) and after 2 ns of equilibration length. This procedure has been applied to each cluster in the range \( 21 \leq N \leq 3095 \), including \( N = 5631 \) and \( N = 6169 \), and except those with sizes \( N_{\text{SC}} = 9437 \) and \( N_{\text{SI}} = 10803 \), where an equilibration length of 1 ns was used. In the equilibration period, the Berendsen’s thermostat with time-coupling parameter \( \tau = 0.4 \text{ ps} \) and target temperature \( T_0 = 298 \text{ K} \) was used. In all the simulations a time-step of 1 fs is used, and periodic boundary conditions have been applied, but with a much larger box length than the cluster radius to ensure noninteracting images. A cutoff radius equal to half box length was used for clusters sizes \( N \leq 87 \); otherwise, a cutoff radius of 2 nm was set. Statistical properties of the produced sampled distribution were obtained using the coarse-graining stratified systematic sampling dividing the sample in equal bins of length 0.05 ps, to avoid serial correlations. The averages of the properties considered in this work are reported at the 95\% confidence level. All simulation results have been obtained using only the CR potential model, because the asymptotic behavior of \( E(N)/N \) for the relaxed SC clusters reproduces very well the experimental cohesive energy used in the parametrization of the model.

As observed from the average equilibrium configurations of the two series of clusters shown in Figure 8, one of the more evident temperature effects on clusters for sizes \( 347 < N < 9437 \) is the smoothing of all the peaks of the tetrahedral pyramidal motifs of the relaxed clusters. This is easy to understand because of the natural tendency of lower coordinated surface atoms to increase its coordination number to the optimum value, which in this case is driven by thermal energy. For the first three clusters of each series, we have found that all the peaks are completely destroyed in agreement with recent results, which show that small gold clusters are low-symmetry or amorphous-like clusters. On the other hand, for two of the largest clusters of each series, Figure 9, some peaks remain mainly because of the 1 ns length used in its equilibration period. Their contribution to the energy can be neglected because, as we will show below, volume contribution dominates over surface contributions at these sizes. Eventually, it is expected that these peaks will be finally smoothed if the equilibration time is extended to 2 ns. Thus, the surfaces of our equilibrated clusters at room temperature for sizes in the range \( 347 < N \leq 10803 \) resemble the TEM images of the gold particles in panels a, b, and e (SEM image) in Figure 2.
By following the equilibration time history of clusters with sizes greater than 347 atoms, we have observed in detail how the peaks of the pyramids are smoothed. For any cluster at the initial steps of the equilibration process, each pyramid tip atom is diffused along one edge and it attaches around the middle edge for a long time, generating metastable states. After a short period, these atoms remove (almost always) other atoms from those mid-edge positions, which are rolled toward the base of the pyramid, and the total energy is stabilized for longer periods, which might be considered as a stable state. For the SC clusters, we have found that those atoms form oscillating pairs of atoms, which are deposited on the surface around vertices connecting square faces. Nowadays, there is high interest in the collective electronic excitations or surface plasmons of star-like gold nanoparticles, and these theoretical findings could give some insight into the features of the collective electronic excitations resulting from the interaction of star-like nanoparticles with the electric field of light.27,29,45,46

From the above results on equilibrated surface atoms, minimal changes in the behavior of the number of surface atoms as a function of cluster size are expected, and this is indeed the case if the curves $N(N)$ for the SC and SI clusters in Figure 6 are compared with those of the equilibrated clusters shown in Figure 10. The behavior of the corresponding curves, for $N > 347$, is very similar. As in the case of the relaxed clusters described in the preceding section, curves in Figure 10 have been obtained by linear fitting $N_{surf}$ to eq 7, where $N_{surf}$ is the number of surface atoms of the average equilibrium configurations shown in Figure 8. The coefficients of the fitting functions for the equilibrated SC and SI clusters are given in Table 4, where the coefficient $\gamma$ has been excluded from the fitting process in order to avoid large asymptotic errors in the coefficients. Because the main interest here is on the large stellated structures which maintain their peaks, the first three equilibrium configurations of each series have been excluded from the fitting, and also from the discussions, because they are amorphous or low-symmetry structures.38,44 $N_{surf}$ has also been computed through the Lee–Richard algorithm39 using a probe radius $r_{probe} = 1.66 \text{ Å}$.

<table>
<thead>
<tr>
<th>$\alpha$</th>
<th>$\beta$</th>
<th>$\gamma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SC</td>
<td>$6.41 \pm 0.02$</td>
<td>$-13.07 \pm 0.33$</td>
</tr>
<tr>
<td>SI</td>
<td>$8.44 \pm 0.03$</td>
<td>$-37.32 \pm 0.50$</td>
</tr>
</tbody>
</table>

By following the same procedure as for the relaxed clusters, we have also explored which type of equilibrated gold cluster is more favorable. In this case, $E$ in eq 9 is the total energy of a cluster of size $N$, $N_{surf}$ is given by eq 7 and Table 4, and for $E_{surf}$ we have used $A_{SI} = -3.7132 \text{ eV/atom}$ given in Table 5. The calculated values for $\Delta SC(N)$ and $\Delta SI(N)$ are given in Figure 11 together with its fitted curves, where the coefficients are given in Table 5. In this case, only $E(N)$ data for $N \geq 347$ have been fitted to eq 8, and to avoid large asymptotic errors in the coefficients, $C$ and $D$ have been omitted in the fitting process of data $E_{SC}(N)$ and $E_{SI}(N)$, respectively. From interpolation and extrapolation results we have found that the SI clusters are more favorable in the range $671 \leq N \leq 224 \text{ 586}$ atoms (see Figure 12), while SI clusters are more favorable out of this range, excluding the first five smaller clusters. Thus, we predict that stellated gold clusters coexist around two crossover sizes, one at $N = 671$ and another one at $N \approx 224 \text{ 586}$, a result that is in good agreement with experimental observations (see Figure 2).

Explanations for the formation of observed stellated clusters (Figures 1 and 2) is still under discussion. From our experimental experience, a fast growth rate is helpful in the formation of particles with anisotropic growth shapes. Some authors argue that the role of ascorbic acid (AC) is crucial in the crystal habit control (from platelets, regular polyhedra, and shapes with anisotropic growth),2,30,47 because AC accelerates the reduction of metal ions, thus increasing the growth rate. But there is evidence that synthesis by DMF-PVP28,29,48 also generates nanostars, and even the role of saccharin in the anisotropic growth mechanism has been discussed.49 Thus, the role that ascorbic acid plays in this type of NP synthesis is currently unclear.

5. Conclusions

We have synthesized and characterized stellated gold nanoparticles by TEM, as well as performed a systematic study of
cuboctahedral or icosahedral clusters with the same magic size; thus, this difference in the number of atoms arises from the tetrahedral motifs attached to their triangular faces.

The present study on stellated gold nanoparticles is driven mainly by fundamental and applied reasons. From a fundamental point of view, we advanced the hypothesis that stellation on clusters (Kepler–Poisson solids) is a process that follows after the nucleation of well-defined structures, such as octahedra and icosahedra (platonic shapes) and cuboctahedra and truncated octahedra (archimedean solids), where each one of these shape classifications could be (although with boundaries which are not well-defined) located in size regions of the cluster growth. From an applied point of view, stellated gold nanoparticles have, nowadays and projected in the near future, potential nanotechnological applications in disciplines such as the biomedical applications (cell tissue imaging, sensing and cancer therapy, drug delivery, etc.)11–14 and nanophotonics applications.27,29,45,46

References and Notes


TABLE 5: Same Title as for Table 3, in this case for the Equilibrated Gold Clusters with the CR Potential Model

<table>
<thead>
<tr>
<th>cluster type</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>SC</td>
<td>$-3.6982 \pm 0.0006$</td>
<td>$1.496 \pm 0.012$</td>
<td>$-1.64 \pm 0.54$</td>
<td>$0.0151$</td>
</tr>
<tr>
<td>SI</td>
<td>$-3.7132 \pm 0.0040$</td>
<td>$2.545 \pm 0.107$</td>
<td>$-8.22 \pm 0.63$</td>
<td>$0.0000$</td>
</tr>
</tbody>
</table>

$\alpha = A - E_{ref}$, where $E_{ref} = \Delta E_{SI}$. 

Figure 11. Same caption as for Figure 7, in this case for the MDS results obtained using the CR potential model;19 the excess energy $\Delta(N)$ has been calculated using the total energy. Note that we have excluded the smallest clusters from the fitting, because they are low-symmetry or amorphous structures with non-star-like shape.

Figure 12. The difference in excess energy or binding energy per $N_{eq}$ of the SC and SI clusters as function of cluster size. The curve is obtained from the fitted curves in Figure 10.