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Size-dependent Strain and Surface Energies of Gold Nanoclusters

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Abstract

Gold nanocluster properties exhibit a unique size-dependence. In this contribution, we employ reactive molecular dynamics simulations to calculate size- and temperature-dependent surface energies, strain energies and atomic displacements for icosahedral, cuboctahedral, truncated octahedral and decahedral Au-nanoclusters. The calculations demonstrate that the surface energy decreases with increasing cluster size at 0 K but increases with size at higher temperatures. Calculated melting curves as a function of cluster size demonstrate the Gibbs-Thomson effect. Atomic displacements and strain are found to strongly depend on the cluster size and both are found to increase with increasing cluster size. These results are of importance for understanding size- and temperature-dependent surface processes on gold nanoclusters.

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1. Introduction

It is well known that nanoclusters (NC's) have different physical and chemical properties compared to their bulk counterparts, due to their large surface-to-volume ratio, their specific geometries and their electronic structure.[1] Additionally, particular structural relaxation and surface reconstruction phenomena of nanoclusters further greatly influence their electronic and optical properties.[2,3]

Gold nanoclusters in particular display unique electronic, optical and catalytic properties. Control over these properties allows their use in a variety of applications, including e.g. nanolithography,[4] nanophotonics,[5,6] catalysis[7-9] and biomedicine.[10] Hence, it is of great importance to understand the structure and stability of gold nanoclusters.

An important descriptor of the solid surface with respect to its reactivity is the surface energy.[11,12] Previously, it has been reported in many studies that modification of the surface energy can lead to a change in particle shape[13-15]. This in turn affects both the kinetics and thermodynamics of processes taking place at the particle surface.[16,17] While the surface tension of liquids has been understood for over 100 years, the surface energy of solids is not nearly as well understood, despite its paramount importance for catalysis, crystal growth, colloidal behavior, sintering, fracture, and essentially every other surface-mediated process.[18] Most of the experimental surface energy studies[19-26] available for solids is doubtful to at least some extent and in poor agreement with each other as well[13,21,27] and often includes uncertainties of unknown magnitude[26]. This makes the computational study of the surface energy very important. Furthermore, metal clusters exhibit unique size-depended properties [7,29,30] and surface energies of nanoclusters are often considered to be of prime importance for their catalytic activity[31]. It is therefore of interest to study the surface energy and closely related surface properties such as strain as a function of cluster size.

At the nanoscale, the most stable structures are the icosahedron, cuboctahedron and decahedron.[31,32] Ino et al. predicted that icosahedral Au clusters should be stable up to sizes of 40000 atoms.[33,34] Previous studies proposed that geometries with {111} surfaces are highly stable and do not melt below the bulk melting temperature, in contrast to structures containing {100} and {110} surfaces.[34-36] In contrast to the icosahedron, however, both the cuboctahedron and the truncated octahedron show the fcc structure, and thus correspond to minimum energy structures for fcc metals such as gold.[37-39] Moreover, the stability of icosahedral clusters decreases significantly with increasing cluster size [34,40-42].

Hence, for the smallest metallic clusters, the icosahedron is the most stable structure, but for larger clusters the cuboctahedron, truncated octahedron and decahedron are more stable.[31,32] Based on a second moment approximation tight binding calculations, Myshlyavtsev *et al.* found that for clusters containing 923 atoms or less the icosahedron is the most stable structure, while the stability crossing with the cuboctahedral structure was found for 561 atoms or less when using the quantum Sutton-Chen potential.[43] This energetic difference between icosahedra and cuboctahedral is generally attributed to balancing the higher surface stability of the {111} facets of icosahedra against the elastic distortion induced by their five-fold symmetry. In smaller clusters, the surface stability dominates, favoring the icosahedral shape, while for larger clusters the elastic distortion dominates, favoring the fcc lattice. Typically, both cuboctahedra and icosahedra contract relative to the bulk atomic positions. With increasing size, this contraction vanishes for cuboctahedra, while it increases with increasing size for icosahedra.[44] The stability of the different polyhedral geometries of the nanoclusters can be determined e.g. by calculating potential energies. For instance Li et al. found that for very small Au nanoclusters the icosahedron is much more stable than Ino-decahedral and cuboctahedral structures. However, their calculations demonstrated that for larger clusters Ino-decahedral clusters are more stable.[31]

The effect of temperature, however, on the surface and strain energies remains an outstanding issue. Previously, surface energy calculations for a pure Au cluster containing 256 atoms at different temperatures reported an increase in surface energy with temperature[45]. Another study carried out to determine size-dependence of surface energies for Au nanoparticles reported a decrease in surface energy against cluster size[13]. Similar studies were also carried out for Ni[12], Ag[2] and Al[46] nanoparticles which also indicated a decrease in surface energy with increasing cluster size. Many molecular dynamics studies were previously carried out to investigate melting of Au nanoclusters, based on different interatomic potentials such as Embedded-Atom Method[47-51], Sutton-Chen potential[52] and many body glue potential[34]. Similarly, there are many studies reporting on the melting behavior of e.g. clusters of Ag[53], Cu[54], Ni[55] and other metals[56,57] using molecular dynamics simulations.

Most of the above stated studies emphasize on the size-dependent melting behavior, rather than the size-dependent surface and strain energies of Au nanoclusters. So, we here report on surface energy calculations for icosahedral, cuboctahedral, truncated octahedral and decahedral gold nanoclusters in a wide range, containing 116 up to 6525 atoms. Since lattice strain can influence the surface energy and the relevant mechanical properties[58], we also calculate the size dependence of the atomic displacements and associated strain.

2. Simulation model and method

Surface energies and strain of the Au-nanoclusters are calculated by classical molecular dynamics (MD) simulations. In a MD simulation, the time trajectories of all atoms in the system are followed through space by integrating the equations of motion. Forces are derived as the negative gradient from a suitable interatomic potential.

We here employ the standard Embedded Atom Method (EAM) potential[59,60] as implemented in the LAMMPS code[61,62] to describe the interatomic interactions. The temperature range investigated is 100 K – 1300 K. Previously, EAM has been used to successfully calculate surface properties of gold nanoclusters[47-51] as well as for other metals[2,55].

We consider 9 icosahedral and 9 decahedral clusters of different sizes (containing N = 147, 309, 561, 923, 1415, 2057, 2869, 3871 and 5083 Au atoms). The each icosahedral cluster has a full-closed surface consisting of 20 close-packed triangular faces corresponding to {111} faces in the crystal lattice. The clusters with this atomic/mass numbers are so-called magic number clusters, which show an increased stability relative to non-magic number clusters. [31,63-66] Similarly, we also consider 5 cuboctahedral (containing N = 309, 923, 2057, 3871 and 6525 atoms) and 5 truncated octahedral (containing N=116, 490, 1288, 2670 and 4796 atoms), where each cluster is cut from the fcc lattice. A graphical representation of these structures is provided in the Supplementary Information.

The surface energy is calculated as[2,12,13,45]

$$E_{surface} = \frac{E_{P,cluster} - E_{P,bulk}}{A_{cluster}} \qquad (1)$$

where $E_{P,cluster}$ is the potential energy of the cluster, $E_{P,bulk}$ is the potential energy of a bulk system containing the same number of atoms, and $A_{cluster}$ is the total cluster surface area. To calculate the surface energy at 0 K, we minimized the structure using the conjugate gradient minimization method[67,68] with a force tolerance of $1.0\text{x}10^{-8}$ eV/Å. For the calculation of the surface energy at non-zero temperatures, MD simulations are carried out in the canonical ensemble. The temperature is controlled by the Nose-Hoover thermostat[69] employing a relaxation constant of 100 fs.

In all calculations, the time step was set to 1 fs and each system was equilibrated for 300 ps prior to analysis. The surface energies at finite temperatures were calculated based on average potentials energies and cluster surface areas, averaging over the final 2000 snapshots of the simulation, corresponding to 2 ps using equation 1. Cluster surface areas were calculated using the qhull code[70,71]. The structural evolution of the nanoclusters during the melting process is analyzed by means of the Ackland-Jones bond-angle method[72], allowing to assign a crystal type (fcc, hpc or bcc) to each atom. Ovito[73,74] software package is used for visualization.

3. Results and Discussion

3.1. Size dependent surface energy of icosahedral gold nanoclusters

Since the surface of an icosahedron consists of {111} facets, while the surfaces of cuboctahedral, truncated octahedral and decahedral clusters are composed of both {111} and {100} facets, we first calculate the surface energy of these facets for an infinite surface. We find values of 0.79 J.m^{-2} for the {111} facet which is in good agreement with the values in the range 0.72 – 0.80 J/m^2 as calculated by Singh-Miller and Marzari[75], Almora-Neyvis et al.[76], Holec et al.[13] and Crljen et al.[77] using Density Functional Theory (DFT) and 0.79 J.m^{-2} and 0.89 J.m^{-2} calculated by Keith et al.[78] using EAM and Modified Embedded Atom Method (MEAM) potentials respectively, to be compared to an experimental value of 1.10-1.50 $J.m^{-2}$ for the {111} facet.[20,79,80]

Similarly, we find a value of 0.92 $J.m^{-2}$ for the {100} facet which is also in reasonable agreement with 0.88 $J.m^{-2}$ and 0.87 $J.m^{-2}$ as calculated by Almora-Neyvis et al.[76] and Holec et al.[13] using DFT, 1.04 $J.m^{-2}$ as calculated by Diao et al.[81] using the MEAM potential and 0.92 $J.m^{-2}$ and 1.08 $J.m^{-2}$ as calculated by Keith et al.[76] using EAM and MEAM potentials, respectively. While the EAM potential thus yields an absolute value for the surface energy too low compared to the experiment, as is also the case for the DFT calculations, the EAM potential correctly predicts the {111} to be the lower energy surface.

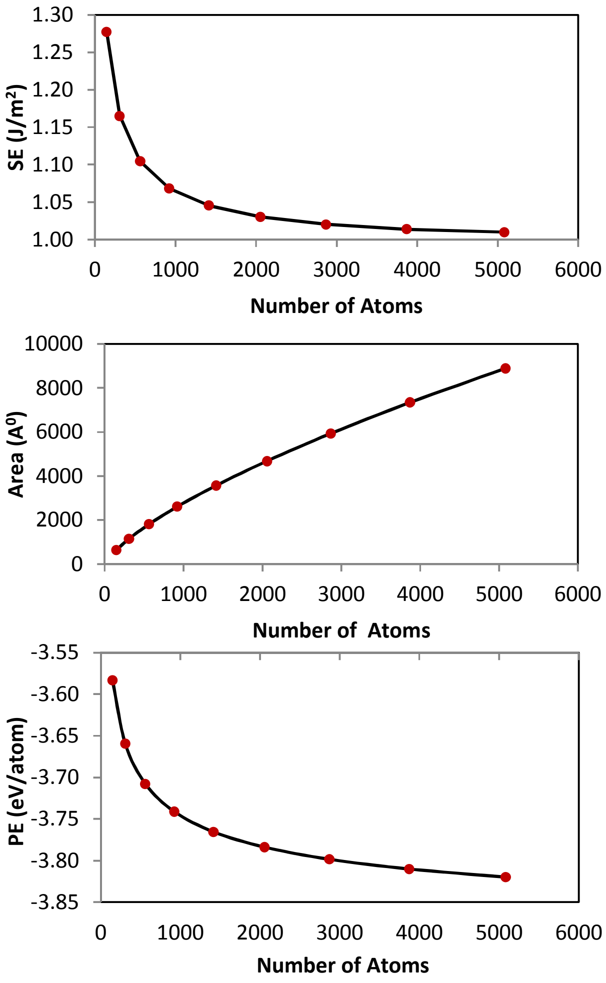


Figure 1 - Calculated surface energies (top panel), surface area (middle panel) and the potential energy per atom (bottom panel) for icosahedral clusters as a function of size.

The calculated surface energies for the icosahedral gold nanoclusters as a function of size at 0 K are shown in Figure 1 (top panel). Figure 1 also shows the cluster surface area and the potential energy per atom for different icosahedral clusters (middle panel and bottom panel, respectively). It can be seen in Figure 1 that the surface energy at 0 K decreases for increasing cluster size. This effect is due to the decrease in surface-to-volume ratio for increasing particle size as shown in Figure 2. Indeed, as the particle becomes smaller, the potential energy per atom decreases (i.e. becomes more negative; see Figure 1, bottom panel) due to the increasing fraction of under-coordinated surface atoms with lower cohesive energy. These results are in line with literature results for surface energies of Ni[12] and Ag[2] nanoclusters. Note that the large surface-to-bulk ratio in nanoclusters is also (in part) responsible of their high chemical reactivity. Indeed, the large fraction of surface, edge and corner sites is in part responsible for an associated change in surface energy.[9,82]

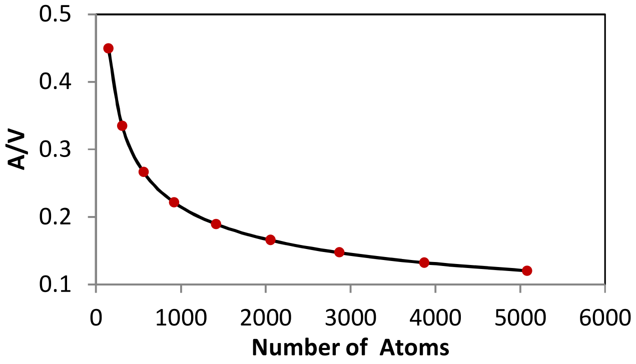


Figure 2 - Calculated surface to volume ratio for the icosahedral clusters as a function of size.

Due to thermal expansion and thermal disorder, however, the surface area and surface energy of a nanocluster are naturally also a function of temperature. In Figure 3, we show the calculated temperature dependence of the surface energy for icosahedral gold nanoclusters containing 561 and 3871 atoms, respectively, in the temperature range 0 – 1300 K. The figure shows a sharp increase in surface energy at 800 K and 900 K for the smaller and larger cluster, respectively, typical for signaling the onset of melting of the clusters. The increase in the onset temperature for melting for the larger cluster compared to the smaller cluster is in agreement with the Gibbs-Thomson effect. The observed trends are similar to earlier reports for melting Au[34,47-51] and other[53-57, 83-84] nanoclusters.

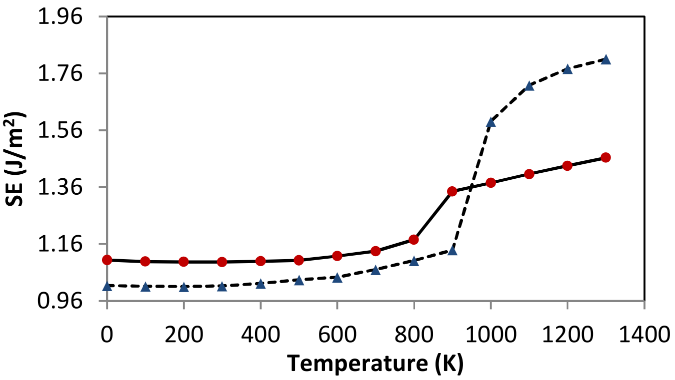


Figure 3 - Comparison of surface energies for the icosahedral clusters Au_{561} (red circles) and Au_{3871} (blue triangles) in the temperature range of 0-1300 K.

Moreover, we also observe a strong increase in surface energy with increasing temperature for the larger cluster, which is larger than in the case of the smaller cluster. Thus, while the surface energy decreases with increasing cluster size at 0 K as shown above, it increases with increasing size at high temperatures. Indeed, the Au_{3871} cluster shows a surface energy at 1300 K of 1.810 J/m^2, to be compared with a lower surface energy of 1.464 J/m^2 for the smaller Au_{561} cluster. Note that the crossing of the surface energies occurs near the melting interval of both clusters. Thus, below the onset of melting, the surface energy of the smaller cluster is larger than the surface energy of the larger clusters, while at temperatures above the permanent and complete melting the order is reversed as shown in Figure 3.

Naturally, also the crystal surface morphology is a strong function of temperature, as shown in Figures 4 and 5 for the Au_{561} and Au_{3871} icosahedral clusters, respectively. It can be seen that the facets on the surface of the icosahedral gold clusters soften, but do not pre-melt below the melting temperature. This softening is due to the increasing mobility of vertex and edge atoms with temperature.[85] As a result, the average shape of the cluster is nearly spherical at the onset of melting.

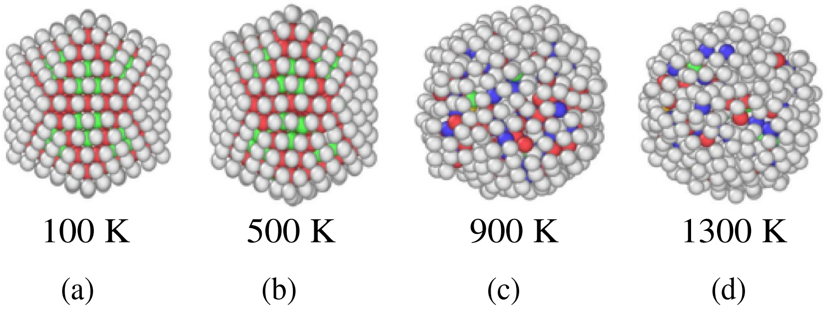


Figure 4 - Icosahedral structure of Au_{561} cluster at (a) T= 100 K (b) T= 500 K (C) T= 900 K (d) T= 1300 K. Green, red and blue represent fcc, hcp and amorphous core, respectively, while white shows other undefined coordinations.

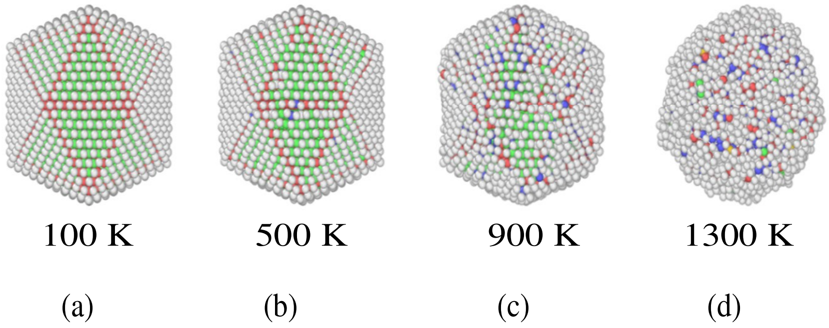


Figure 5 - Icosahedral structure of Au_{3871} cluster at (a) T= 100 K, (b) T= 500 K, (c) T= 900 K and (d) T= 1300 K. Color coding is the same as in Figure 4.

We also performed a bond-angle analysis to gain insight in the possible change in crystal structure upon heating. This analysis demonstrates that in both Au_{561} and Au_{3871} the local coordination of the atoms in the particles changes quite siginificantly with temperature. Specifically, at 100 K, the Au_{3871} cluster contains 43.4% atoms in fcc configuration and 30.7% atoms in hcp configuration. At 1300 K, however, these numbers drop to only 1.2% and 14.6% for fcc and hcp, respectively. Moreover, there are no amorphous core at 100 K, increasing to 11.4%

at 1300 K. A similar result is also found for the Au_{561} cluster, i.e., the number of atoms in fcc and hcp coordination decreases with temperature, while the fraction of amorphous core atoms increases.

There are different methods for analyzing nanoclusters melting, including e.g. calculating a suitable order parameter such as the Lindemann index[86] calculating the free energies of solid and liquid states employing standard thermodynamic integration, or calculating the radial distribution function (RDF).[87,88]. We here consider the RDF along with the caloric curve to analyse the melting behavior of the considered clusters, similar to earlier MD studies on Au nanocluster melting[78].

Figure 6 shows the variation of RDF with temperature. While the crystallinity can be clearly seen at 100 ^{0}C for both Au_{561} (b) and Au_{3871} (a), the sharp peaks indicative of a crystalline structure dissappear with rising temperature. At a temperature of around 900 ^{0}C, the peaks spread out, indicative of melting.

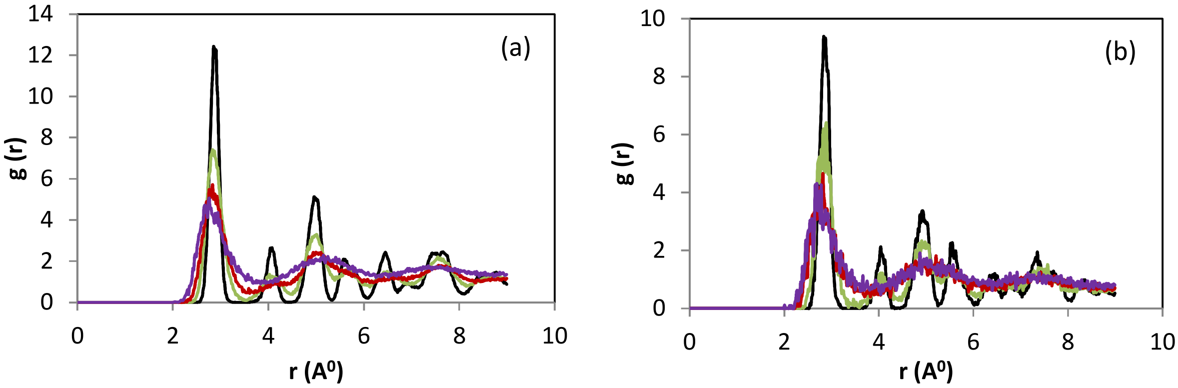
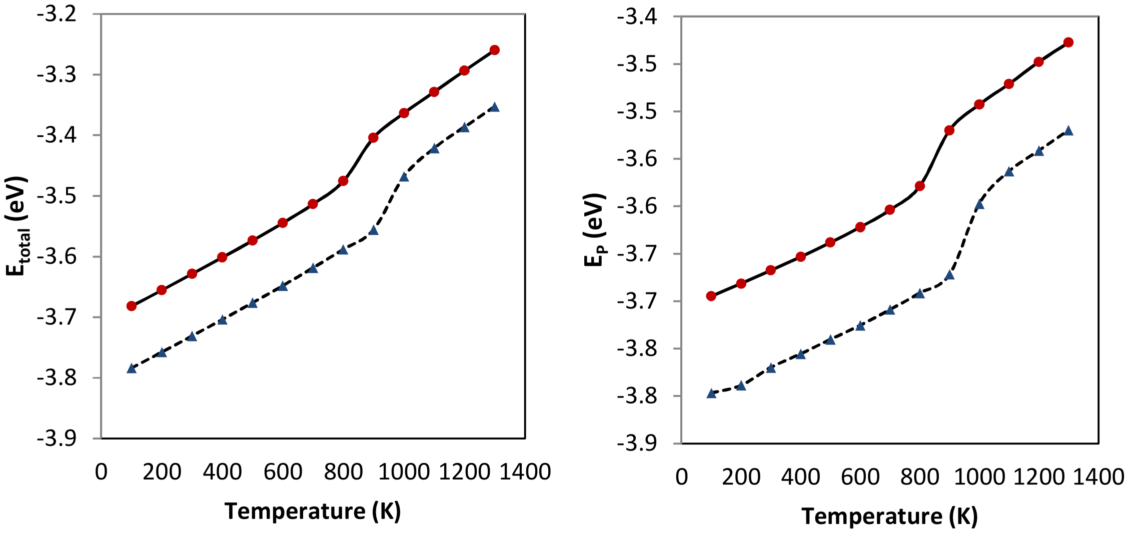


Figure 6 – The radial distribution function of the icosahedral clusters Au_{3871} (a) and Au_{561} (b) at 100 (black), 500 (green), 900 (red) and1300 K (purple).

This corresponds to the calculated caloric curves as shown in figure 7. A sharp increase in energy can be seen at 800 K and 900 K for the smaller (a) and larger (b) cluster, respectively, typical for signaling the onset of melting of the clusters.



(a) (b)

Figure **7**– (a) Caloric curve for the icosahedral cluster Au_{561} (red circles) and Au_{3871} (blue triangles) (b) Potential energy curves for the icosahedral cluster Au_{561} (red circles) and Au_{3871} (blue triangles) as a function of temperature in the range 0-1300 K

3.2. Surface Energy of Cuboctahedron, Truncated Octahedron and Decahedron Gold Nanoclusters

Similar to the results shown above for the icosahedral clusters, the surface energies of cuboctahedral, truncated octahedral and decahedral clusters at 0 K are found to decrease with increasing cluster size as shown in Figure 8. For a given number of atoms, cuboctahedral clusters show a slightly higher surface energy than the icosahedra in the case of the smaller clusters (Au_{309}, Au_{923}), while for bigger clusters (Au_{2057}, Au_{3871}), the decahedra are found to have a slightly lower surface energy. This is shown in Figure 9. This effect is caused by the stability of the clusters as discussed above. Indeed, for smaller clusters icosahedra are more stable while for larger clusters decahedra are most stable. This result is in line with earlier literature reports.[31]

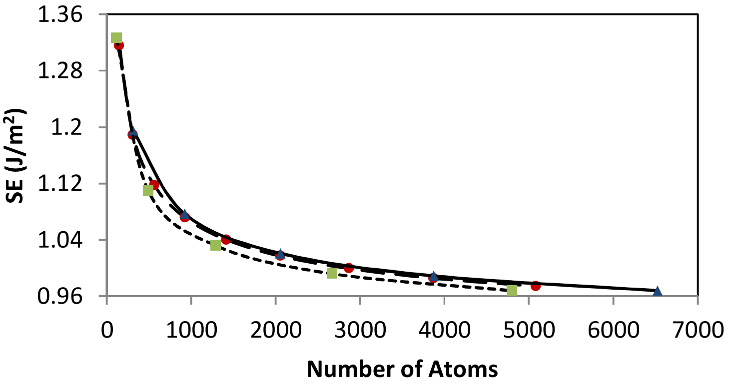


Figure 8 - Calculated surface energies for different cuboctahedra (blue triangles), truncated octahedral (green squares) and decahedra (red circles).

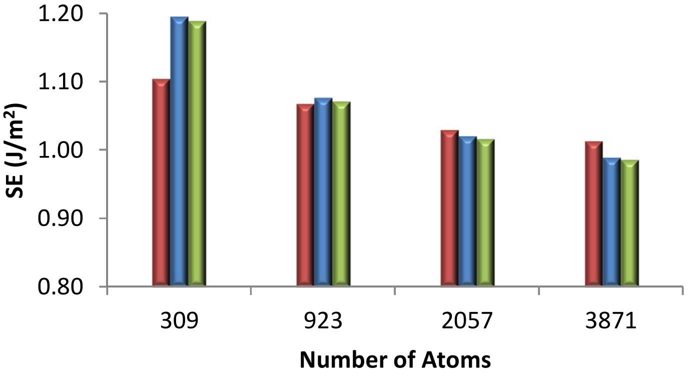


Figure 9 - Calculated surface energies for icosahedron, cuboctahedron and decahedron clusters containing the same number of atoms. Red, blue and green bars indicate icosahedral, cuboctahedral and decahedron structures, respectively.

As shown in Figure 10, we also compared our surface energy calculations to calculations employing the Modified Embedded Atom Method (MEAM) and calculations at the tight-binding

(TB) level, using the potential developed by Cleri and Rosato.[89] The latter potential was previously used to describe the behavior of a number of thermodynamic characteristics of Au and other fcc metals.[90] While the MEAM potential gives a slightly higher value for the surface energy, and the TB potential gives a lower surface energy, the observed trend in the three calculations confirms the decreasing surface energy with increasing cluster size.

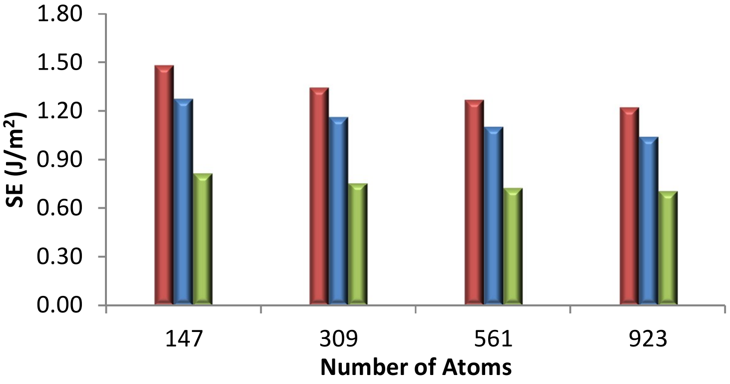


Figure 10 - Comparison between different potentials for surface energy calculation of icosahedral clusters. Red, blue and green bars indicate MEAM, EAM and TB_SMA potentials, respectively.

3.3. Displacement and Strain calculation

As mentioned above, strain and strain energy are also important descriptors for nanoclusters, in particular in relation to their reactivity. We therefore also calculate the strain, strain energies, and atomic displacements in icosahedral, cuboctahedral and truncated octahedral clusters as a function of cluster size.

$$E_{strain} = E_{unrelaxed} - E_{relaxed} \quad (2)$$

Strain energies are calculated by equation (2) where $E_{relaxed}$ is the potential energy of the cluster after minimization and $E_{unrelaxed}$ is the potential energy of the cluster with all atoms in their ideal lattice positions. The minimum energy structure (i.e. the relaxed structure) is considered as the reference structure.

$$\varepsilon = \frac{\Delta D}{D} \qquad (3)$$

We calculate the strain by equation (3)

where D is the diameter of the cluster in its minimum energy structure and ΔD is the change in this dimension upon positioning the atoms in their ideal bulk positions.

Figure 11 shows the strain energy per atom for icosahedral, cuboctahedral, truncated octahedral and decahedral clusters as a function of size at 0 K. With increasing size, a continuous increase in strain energy is observed for icosahedral clusters, while a continuous decrease in strain energy (i.e., towards zero) is observed for cuboctahedral and truncated octahedral clusters. Therefore, perfect icosahedra become increasingly less stable with increasing size due to the elastic distortion associated with their five-fold symmetry. Cuboctahedra and truncated octahedral, on the other hand, increasingly resemble the fcc bulk structure with increasing size. Moreover, with increasing size, the importance of the surface energy (which is higher for the cuboctahedral clusters, due to the presence of the {100} facets) decreases, since the fraction of surface atoms decreases with increasing cluster size. Therefore, the smallest clusters assume the icosahedral configuration while larger clusters will adopt the fcc configuration.

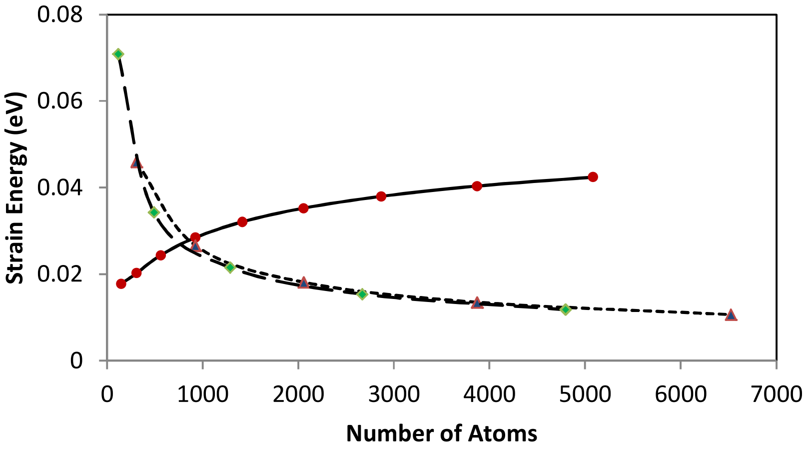


Figure 11 - Strain energy calculations for different icosahedral (red circles), cuboctahedral (blue triangles) and truncated octahedral (green squares) Au clusters.

Figure 12 shows the calculated volumetric strain and atomic displacements for the icosahedral Au_{309} nanocluster (NC). The colors represent the strain values. Interestingly, it can be seen that atoms at edges and corners are relaxing with inward displacements while terrace atoms are displaced outwards. Similarly, shorter and stronger bonds for under-coordinated atoms in comparison to those between fully coordinated atoms in the bulk have been reported,[91,92] which is in line with our observation of contraction of vertex atoms compared to the expansion of face atoms in nanoclusters. Moreover, for smaller cluster there are more under-coordinated atoms (and hence stronger bonds) and therefore a higher surface energy compared to larger clusters at 0 K.

Thus, the clusters are observed to assume a rounded shape upon relaxation, which is in agreement with experimental observations.[58,93] Moreover, edges and corners are found to relax with larger displacements, corresponding to a larger lattice strain, compared with the center position. Again, this observation is consistent with experimental results.[58,93]

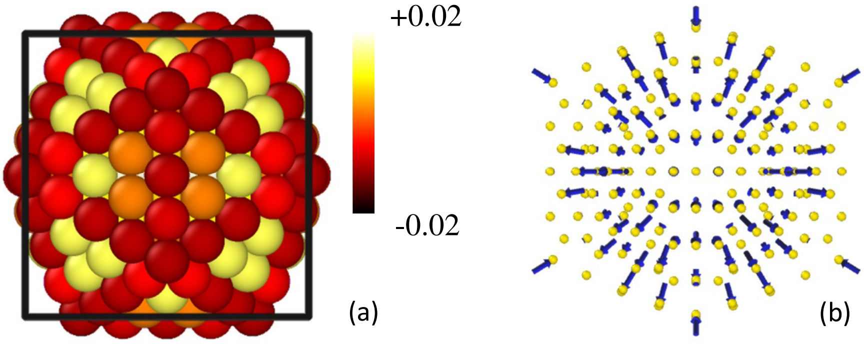


Figure 12- (a) Calculated volumetric strain for the icosahedral Au_{309} cluster. While atoms in the center of the faces move outwards ("expand") as indicated by the yellow colouring, corner and edge atom move inwards ("contract") as indicated by the dark red colouring. (b) Calculated displacement vectors, showing inward displacement of vertex atoms and outward displacement of face atom.

Finally, the strain also strongly depends on the cluster size and increases with increasing size. This is shown in Figure 13, calculated both for face-to-face and vertex-to-vertex distances. Note that since the vertices of icosahedra are displaced inwards upon relaxation, negative strain values are obtained in this case, while the face atoms displace slightly outwards upon relaxation, such that in this case positive strain values are obtained. It can be seen that the icosahedra show an increasing expansion in the direction normal to the faces with increasing size, and a vanishing contraction along the direction of the connection line between any two opposite vertex atoms. In cuboctahedral and truncated octahedral clusters, in contrast, face atoms and vertex atoms both tend to zero contraction upon increasing cluster size.

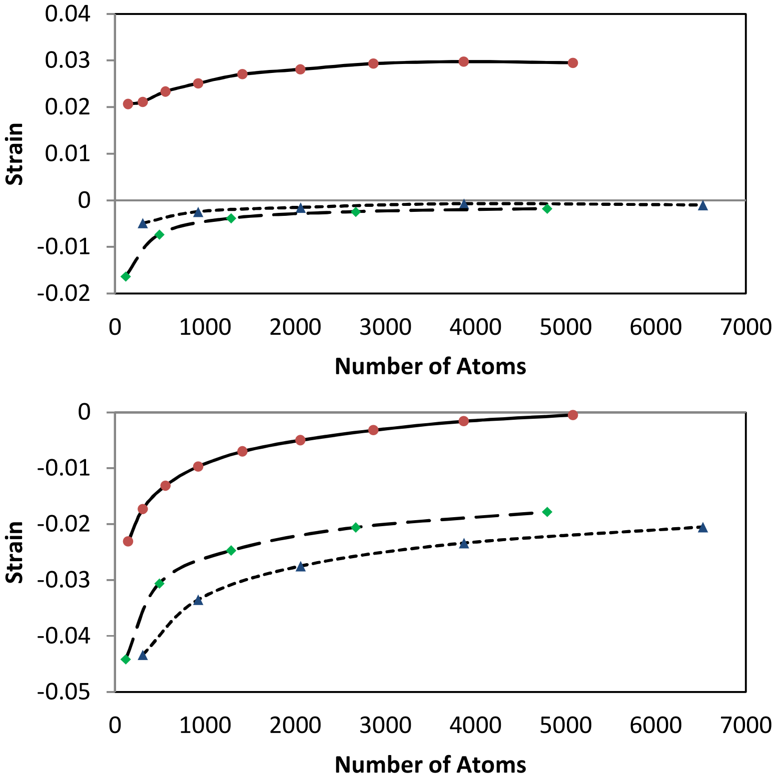


Figure 13- Strain calculations based on face-centered atoms (top panel) and vertex-atoms (bottom panel) for icosahedral (red circles), cuboctahedral (blue triangles) and truncated octahedral (green squares) Au clusters, as a function of size.

Conclusions

We have calculated surface energies, atomic displacements, strain and strain energies for icosahedral, cuboctahedral, truncated octahedral and decahedral Au nanoclusters of different sizes, which is of importance in characterizing these clusters and understanding their physical chemical properties. The results show that the surface energy decreases with cluster size at 0 K but increases at higher temperatures after melting. Typical melting point curves as a function of cluster size are also calculated, demonstrating the Gibbs-Thomson effect. Atomic displacements are found to strongly depend on the cluster size, showing an increase in absolute value with increasing size. Also the strain is found to increase with increasing cluster size, thus tending to zero for negative strain and increasing in absolute value for positive strain. While for icosahedral clusters the strain energy is found to increase with increasing cluster size, the opposite trend is observed for both cuboctahedral and truncated octahedral clusters. Our study shows that all investigated properties are strongly dependent on the cluster size. These results are of importance for understanding size-dependent surface properties and processes of Au nanoclusters.

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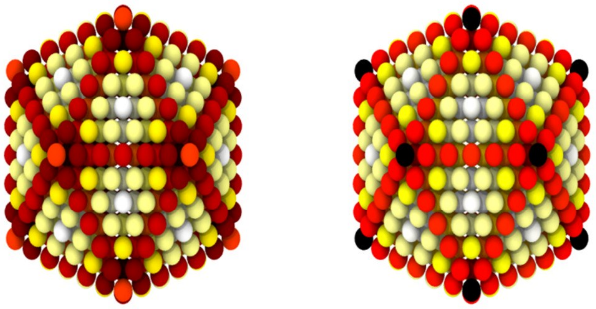
Table of Contents Image



Displacement magnitude volumetric strain

Calculation of size-dependent strain and surface energies of gold nanoparticles