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Wulff construction and molecular dynamics simulations for Au nanoparticles

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Abstract: We present a computational study for the relaxation and thermal stability of the equilibrium shape of gold nanoparticles. We check the stability of the nanoparticles, as they were predicted using DFT calculations and the Wulff construction method, using molecular dynamics (MD) simulations. The nanoparticle shape is found to be robust up to quite high temperatures. Au-Au interlayer distances are found to be smaller in the nanonaparticle than in bulk gold, as expected.

Key words: Gold nanoparticles, Wulff construction, Molecular Dynamics, EMT, ASAP

Nomenclature:

G	Gibbs energy (eV)
γ	Surface tension (J/m^2)
A	Surface area (m^2)

1. Introduction

It is well known that most properties of metal nanoparticles are size-dependent, and that particles with sizes well above the nano-regime have few differences from the bulk material. In addition to size, shape of Au nanoparticles has a key role in their functionality. Examples include sensors [1], biolabels, [2], plasmonics [3] and photonics [4]. Gold nanoparticles often exist in their equilibrium shape, that is the shape that minimizes their total Gibbs energy. The latter is given by

$$G = G_{bulk} + \sum A_{hkl}\gamma_{hkl}, \quad (1)$$

where the first term is the free energy of the bulk material and is constant for constant size of the system. A_{hkl} is the total area of faces parallel to (*hkl*) plane of the crystal, and γ_{hkl} is the surface tension, i.e. the energy required to create a surface of unit area that is parallel to the (*hkl*) plane of the crystal. Under thermodynamic equilibrium, the shape is a polyhedron enclosed by faces of various (*hkl*) crystal orientations.

In the past, we have developed a method to predict the equilibrium shape of metal nanoparticles based on surface tensions calculated from first principles [5-

14]. In these studies, atomistic models were shown to agree with available experimental data even for small nanoparticles, far from the thermodynamic limit. Here, we take a step further and check the validity of this approach. In particular, we are interested in any changes that might exist between the atomistic Wulff construction and the relaxed nanoparticle in terms of (a) relaxation of atomic positions and (b) stability at elevated temperatures.

2. Computational method

In order to check the stability of the shape of gold nanoparticles in nonreactive environment, we perform molecular dynamics (MD) simulations, as they are implemented in the Atomic Simulation Environment ASAP/ASE packages [15,16].

The interatomic interactions are described using the Jacobsen empirical potential functions, based on the semi-empirical effective-medium theory for metals and alloys [17,18]. A detailed comparison of this potential to other interatomic potentials can be found in Ref. [19]. In this approach, the potential energy of the system is equal to the sum of the potential energies of all pairs of atoms in the system, φ_2, which in turn is expressed as $\varphi_2 = \sum_i E_c(\bar{n}_\iota) + E_{AS}$, where $E_c(\bar{n}_\iota)$ is the cohesive energy, given by:

$$E_c(\bar{n}_\iota) = E_0 + E_2\left(\frac{\bar{n}_\iota}{n_0} - 1\right)^2 + E_3\left(\frac{\bar{n}_\iota}{n_0} - 1\right)^3. \qquad (2)$$

E_{AS} is the difference in the electrostatic and exchange-correlation energy in the system of interest and in the reference system. This so-called atomic-sphere correction is given by a pair-potential approximation:

$$E_{AS} = \alpha n_0 \sum_i \left(E_{AS}^{(1)}(i) - E_{AS}^{(2)}(i)\right), \qquad (3)$$

where,

$$E_{AS}^{(1)}(i) = \left[\frac{1}{12}\sum_{j\neq i} e^{-\eta_2(r_{ij}-\beta s_0)}\right]^{\eta/(\eta+\eta_1)},$$
$$E_{AS}^{(2)}(i) = \frac{1}{12}\sum_{j\neq i} e^{-\eta(r_{ij}/\beta - s_0)}, \qquad (4)$$
$$\bar{n}_\iota = n_0 E_{AS}^{(1)}(i).$$

The so-called neutral sphere radius, s_0, is the radius of a sphere around each atom within which the charge is zero. The other parameters are $\beta = (16\pi/3)^{1/3}, \eta_2 = (\eta + \eta_1)/\beta$. Values for the parameters for Au are given in Table 1.

Table 1 The EMT parameters for Au.

Parameter	Value
n_0	0.00703 a_0^{-3}
s_0	3.00 a_0
η	2.53 a_0^{-1}
E_0	-3.80 eV
η_1	0.5 a_0^{-1}

The atomistic models are obtained by means of a hierarchical multi-scale method: First, we perform DFT calculations for the surface energies of gold cleaved in more than 30 crystallographic planes. Second, we use these values in a Wulff construction code and find the equilibrium shape. Third, this polyhedron is filled with Au atoms; due to the finite size of Au atoms, particles of different sizes might have slightly different shapes, as each face of the Wulff polyhedron must accommodate an integer number of atoms. This method has been described in detail in Refs. [5] and [7].

These nanoparticles are annealed at 600 K and then equilibrated at near zero temperature, using molecular dynamics in the constant temperature, pressure and number of atoms (NPT) ensemble, as implemented in the ASAP package.

3. Results and discussion

In Figs. 1 and 2, we present the equilibrium shape of two typical gold nanoparticles, before and after long relaxation at room temperature, followed by annealing at 600 K.

Gold nanoparticles with diameters below 16.3 nm have relatively simple equilibrium shapes [5]. Their shape is an irregular truncated octahedron that exposes mostly hexagonal (111)-like faces. About 15% of its total surface area consists of square (100) faces. A typical such nanoparticle is shown in Fig. 1(a).

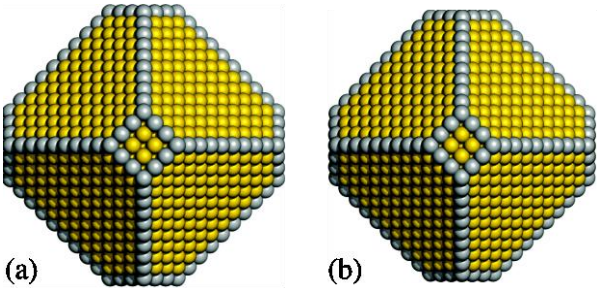

Fig. 1 Equilibrium shape of a gold nanoparticle with initial diameter of 5.0 nm. (a) Initial structure and (b) final structure after equilibration using NPT dynamics. Step and kink atoms are shown in darker color.

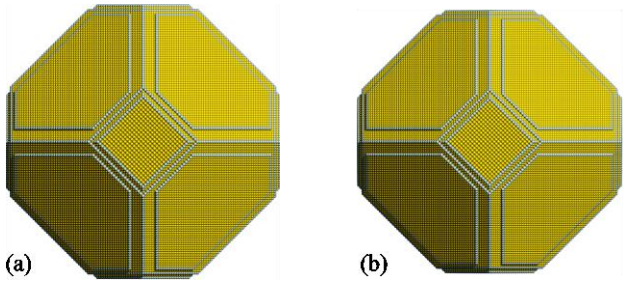

Fig. 2 Equilibrium shape of a gold nanoparticle with initial diameter of 25.1 nm. (a) Initial structure and (b) final structure after equilibration using NPT dynamics. Step and kink atoms are shown in darker color.

For larger gold nanoparticles, there is room to fit more complex crystal orientations found in the Wulff construction for the thermodynamic limit [5]. At diameters above 16.3 nm, edges between (111) and (100) become rounded and are decorated by (332) and (211) surfaces, thus resulting in a higher content of step-edge- and kink atoms. A typical example is shown in Fig. 2(a).

After performing the NPT dynamics, the shape of the nanoparticles remains unchanged, identical to the one predicted using the Wulff construction method. The similarity of the structures before and after annealing reveals that the shape predicted using DFT calculations together with Wulff construction method is indeed in equilibrium state and thus stable. For example, the diameter for the nanoparticle shown in Fig. 1 was found to decrease slightly from 5.0 nm to 4.8 nm. For the larger nanoparticle, the diameter shrinks from 25.1 nm to 24.2 nm. In both cases, the ideal nanoparticle shrinks by about 4%.

This shrinking is mainly due to the relaxation of the outmost layer of Au towards the center of the nanoparticle. For the small nanoparticle shown in Fig. 1, the distance between the two outer layers of the (111) face of was found at 2.30 Å, while for the larger nanoparticle shown in Fig. 2 the same distance measures 2.27 Å. For comparison, the distance between (111) planes in bulk Au, which is 2.41 Å.

This relaxation of the surface layer is a common effect observed in all metal surfaces. To check how this relaxation is consistent with that of an infinite (111) surface, we simulate a slab of Au with (111) surfaces. In that case, we find that the distance between the surface layer of atoms and the second layer is 2.16 Å, a bit higher that that found for the nanoparticle. This difference can be attributed to the finite size of the nanoparticle, where different faces compete. As it is expected, interlayer distances for the larger nanoparticle are closer to the interlayer distances for an infinite slab compared to the same distances in the smaller nanoparticle.

Finally, we verify that the nanoparticles are thermally stable up to temperatures of several hundreds of degrees above room temperature. We observed no change in the structural properties when changing the annealing temperature.

4. Conclusions

The atomistic Wulff construction method has been proved a reliable way to construct computer models of gold nanoparticles. We simulated directly such nanoparticles using state-of-the-art molecular dynamics. The Wulff construction is extremely accurate description of the nanoparticles. The only difference between unrelaxed and relaxed structures is a small overall shrinking of the order of 4%. This effect is attributed to the relaxation of the surface layer of gold atoms. The nanoparticles are stable even at elevated temperatures.

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