

# Empirical Two- and Three-particle Potentials in Application to the Structure of Ag Microclusters on the Surface

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## Abstract

Ag microclusters on the surface are considered. Interaction of the atoms in the cluster is modelled by the three-particle potential introduced by J. N. Murrell. Interaction of the atoms in the cluster with the surface is modelled by Lennard-Jones potential. Number of the atoms in the cluster is varying from 4 to 13. It is shown how interaction with the surface changes the structure of the cluster determined without taking this interaction into account.

The interaction with the surface affects especially the structure of the clusters with 4, 5 and 6 atoms leading in some cases to the complete change of structure with the tendency for all the atoms to be situated on one plane. This tendency is valid for larger clusters as well, but in this case the original structure is more stable and is only partly deformed.

## Introduction

The total interaction energy of the system of N atoms can be generally written as many particle expansion

$$\Phi = \varphi_2 + \varphi_3 + \dots + \varphi_n \dots, \quad (1)$$

where  $\varphi_2, \varphi_3, \dots, \varphi_n, \dots$  are consequently two-, three-, n-body terms:

$$\varphi_2 = \sum_{i>j} U_{ij}, \quad (2)$$

$$\varphi_3 = \sum_{i<j} W_{ijk} \quad (3)$$

and so on. The expressions for the functions  $\varphi$  and the question about the number of the terms in the expansion series have been widely discussed in literature.<sup>1,2</sup> In the last years some empirical and semi-empirical functions were proposed for the two- and three-body interactions, these functions gave a possibility to describe the different solid state properties adequately.<sup>1-7</sup>

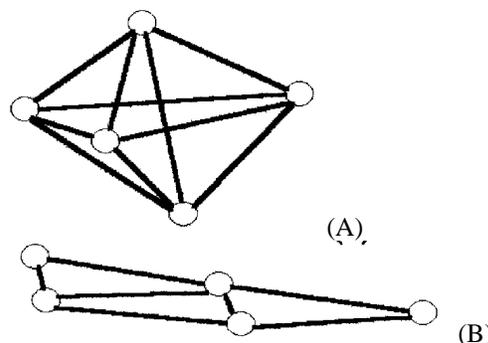


Figure 1. 5-atom case. Trigonal bipyramid with an axis parallel to the support's plane. Here and below (a) means the absence of the support (b) corresponds to the support's presence.

In the papers [8-15] simple two- and three-body potential functions were proposed for monoatomic solid bodies with cubic symmetry including both metals (alkaline metals, noble metals, aluminium, iron) and nonmetals (silicon). With the use of these functions lattice energies, lattice constants, phonon frequencies, elastic constants have been calculated for these substances. It was suggested that these potentials could be used also to describe melts, defect and surface structure and properties of microclusters.

In paper [15] two- and three-body potential functions of metals (Au, Ag, Cu) with the parameters obtained by the comparison with the experimental data on phonon spectra, elastic constants and cohesion energies were used to investigate the microcluster properties of these substances. In particular, the structures with the minimum of energy for microclusters with the number of atoms from three to seven were determined. A bit earlier the same problem was considered for Au and Ag<sup>16</sup> using another empirical potential with two- and three-body terms. However, as was stated in [15], 2 times lower values of the elastic constant were obtained in this paper. In both approaches the electronic structure of the clusters was not taken into account.

It should be noted that the clusters of noble metals have drawn an attention both of theorists and experimentators (see, e.g. [17, 18]). The properties of these clusters on different surfaces can be investigated by different experimental techniques (microscopy, electron diffraction, spectroscopy).<sup>19,20</sup> From a point of view of scientific photography the silver microclusters on the silver halide

surface are of special interest as playing the decisive role in latent image formation.<sup>21,22</sup> Of great importance are such characteristics as mobilities of the clusters and their interaction with defects.<sup>23</sup>

The theoretical calculations of electronic levels, ionization potential, electron affinity and bonding energy for silver clusters on the silver halide surface was carried out in papers [24-26]. It should be noted that it is very difficult to estimate the precision of these results due to difficulty to determine the influence of the used approximations.

In this paper we will consider the influence of the interaction with the support on the equilibrium configuration of small silver clusters (the role of the support can be played by the silver halide). We will use the potential suggested in [15] with two- and three-body interactions between the atoms in the cluster, the interaction between the cluster and the support will be modeled in the "zero" approximation by the surface Lennard-Jones potential.<sup>28</sup>

### The potentials

The two- and three-body potentials of the interaction between silver atoms in the cluster are taken following paper [15]. The pair potential is a Rydberg potential

$$U_{ij} = -D(1+a_2\rho_{ij})\exp(-a_2\rho_{ij}) + \exp[-50(\rho_{ij} + 0.2)],$$

where  $D$  is two-body dissociation energy,  $a_2$  is the the pair potential parameter,  $\rho_{ij}$  is the reduced interatomic distance

$$\rho_{ij} = (r_{ij} - r_e)/r_e, \quad (4)$$

$r_e$  is the equilibrium distance of the two-body potential.

The three-body potential has the form

$$W_{ijk} = DP(Q_1, Q_2, Q_3)\exp(-a_3 Q_1), \quad (5)$$

where  $a_3$  is a three-body potential parameter and  $P(\bullet)$  is a totally symmetric polynomial in the symmetric coordinates  $Q_1$  ( $1 \leq i \leq 3$ ) for the permutation of the three indistinguishable particles

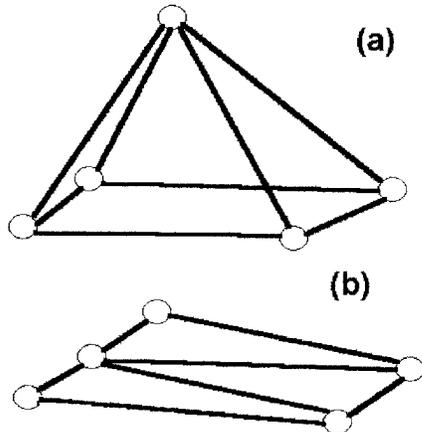


Figure 2. 5-atom case. Pyramid with a plane of the base parallel to the support.

$$\begin{bmatrix} Q_1 \\ Q_2 \\ Q_3 \end{bmatrix} = \begin{bmatrix} (1/3)^{1/2} & (1/3)^{1/2} & (1/3)^{1/2} \\ 0 & (1/2)^{1/2} & -(1/2)^{1/2} \\ (2.3)^{1.2} & -(1.6)^{1.2} & -(1.6)^{1.2} \end{bmatrix} \begin{bmatrix} \rho_{ij} \\ \rho_{ik} \\ \rho_{jk} \end{bmatrix} \quad (6)$$

The polynomial  $P(\bullet)$  is quartic:

$$\begin{aligned} P(Q_1, Q_2, Q_3) = & c_0 + c_1 Q_1 + c_2 Q_1^2 + c_3 (Q_2^2 + \\ & + Q_3^2) + c_4 Q_1^3 + c_5 Q_1 (Q_2^2 + Q_3^2) + \\ & + c_6 (Q_1^3 - 3Q_3 Q_2^2) + c_7 Q_1^4 + \\ & + c_8 (Q_1^2 (Q_2^2 + Q_3^2) + c_9 (Q_2^2 + Q_3^2)^2 + \\ & + c_{10} Q_1 (Q_3^3 - 3Q_3 Q_2^2). \end{aligned} \quad (7)$$

The coefficients in the polynomial were determined in [15] by the comparison With the elastic constants and chosen phonon frequencies for the face-centered cubic lattice and had the following values:

$$a_2 = 6.0, a_3 = 5.5, D = 0.6208 \text{ eV},$$

$$r_e = 2.8792 \text{ \AA},$$

$$c_0 = 0.3872, c_1 = 2.3220, c_2 = 4.4846,$$

$$c_3 = -3.3658, c_4 = -4.4065, c_5 = -8.8459,$$

$$c_6 = 1.7918, c_7 = -3.3523, c_8 = 9.4557,$$

$$c_9 = 3.4883, c_{10} = -10.2426.$$

The equilibrium configurations of the silver clusters with the number of atoms from three to seven without support's influence are given in [15].

We will model an interaction of the atoms in the cluster with the support following [27,28]. Generally this interaction can be written as follows:

$$U(\mathbf{r}) = \sum_{\alpha} \sum_{\mathbf{g}} u_{\mathbf{g}}(z_{\alpha}) \exp(\mathbf{i}\mathbf{g}\boldsymbol{\tau}), \quad (8)$$

where summing over  $\alpha$  means summing over the planes parallel to the surface ( $\alpha = 1$  corresponds to the surface),  $z$  is a distance from the atom to the corresponding layer, a vector  $\mathbf{X}$  determines the position of the support's atom on the plane,  $\mathbf{g} = n_1 \mathbf{b}_1 + n_2 \mathbf{b}_2$ ,  $\mathbf{b}_1$  and  $\mathbf{b}_2$  are the base vectors of the two-dimensional reciprocal lattice.

As an initial approximation we will neglect the effects of charge redistribution between the cluster and the solid bulk and will model the interaction between the cluster and the surface by the Lennard-Jones potential<sup>28</sup>:

$$\begin{aligned} \mathbf{u}(\mathbf{r}) = & 2\pi\epsilon/a \sum_{\alpha} \{q(\sigma^{12}/z_{\alpha}^{10} \sigma^6/z_{\alpha}^4) + \\ & + \sum_{\mathbf{g} \neq 1} \sum_{k=1}^q \exp[\mathbf{i}\mathbf{g}(\mathbf{m}_k + \boldsymbol{\tau})][\sigma^{12}/30 (g/2z_{\alpha})^5 K_5(gz_{\alpha}) - \\ & - 2\sigma^6 (g/2z_{\alpha})^2 K_2(gz_{\alpha})]\}, \end{aligned} \quad (9)$$

where  $q$  is a number of atoms in the elementary surface cell,  $a$  is the cell's area,  $\mathbf{m}_k$  determines the atom's position in this cell,  $K_n$  is the  $n$ -type special Bessel function,  $\sigma$  and  $\epsilon$  are the Lennard-Jones potential parameters.

Further, we will use a well-known and widely used approximation, when a summation over the two-body interactions is substituted by all integration and when only surface atomic layer is taken into account,<sup>28</sup> so we will limit ourselves by the case  $\alpha = 1$ . We will consider the cluster situated sufficiently far from the surface so, we can use the Bessel function asymptote. With these approximations we have the following potential<sup>28</sup>:

$$u(r) = 2\pi\epsilon\rho^*A^6/3 [2A^6/15z^{*9} - 1/z^{*3}], \quad (10)$$

where

$$\rho^* = \mathbf{qa}/\Delta z, \quad z^* = z/a,$$

are dimensionless parameters,  $a$  is elementary cell spacing and  $A = \sigma/a$ .

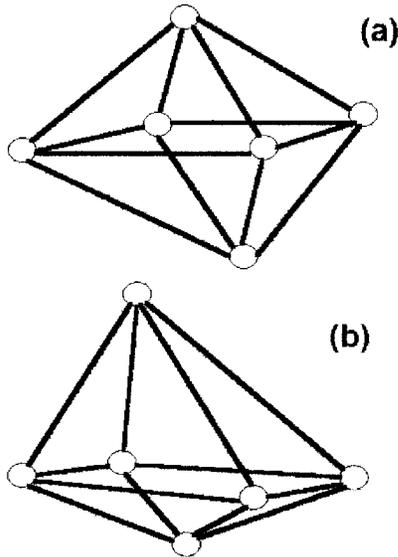


Figure 3. 6-atom case. (Octahedron with 4-th order axis along a perpendicular to the support as surface).

The considered approximations give a possibility to estimate qualitatively an influence of the interaction with the support on the cluster's structure.<sup>29</sup>

The equilibrium configurations of the clusters were determined by the minimizing the total interaction energy as a function of atom's position in the cluster by the Fletcher-Powell method. The parameters were chosen in the intervals 1-2, 1-1.5 and were fixed.

## Results and discussion

Let us consider now in what way the equilibrium structure of silver clusters is changed when the interaction with the support, given by (10), is taken into account.

**Ag.4.** It is quite natural that the structures of possible plane clusters parallel to the support's surface will not change. But if take a tetrahedron with a vertex directed to or from the surface, the interaction with the surface will change a distance between this vertex and a plane made by the three other atoms.

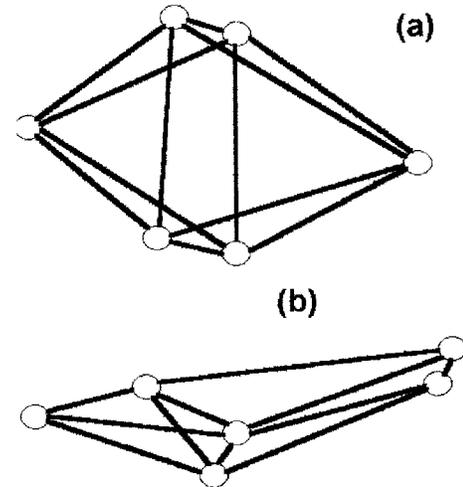


Figure 4. 6-atom case. Octahedron with a 2-nd order axis along a perpendicular to the support's surface.

**Ag.5.** If a trigonal pyramid with an equatorial plane parallel to the support's plane is taken as an initial configuration then the interaction considered will change the pyramid's heights. But in the case when the support's plane is parallel to the bipyramid's axis (fig.1a), the result is nontrivial, the minimum of the energy will correspond to a plane trapezoid with a plane parallel to the support's surface (fig. 1b).

The similar trapezoid can be obtained from the pyramid with a base whose plane is parallel to the support's surface (fig.2a, 2b). It is interesting that such a configuration was obtained in [15] in the absence of the support as energetically not preferable.

**Ag.6.** An octahedron with an axis of 4-th order along a perpendicular to the support's surface (fig. 3a) deforms along this axis as shown on fig. 3b. When an octahedron's axis of the 2-nd order is perpendicular to the surface (fig. 4a), then the energetically preferable configuration is nearly plane (fig. 4b). The same situation occurs for a pentagonal pyramid (fig. 5a), As a result of the interaction with the support all 6 silver atoms occur practically in one plane, parallel to the surface (fig. 5b).

**Ag.8.** To an equilibrium configuration in this case corresponds a cluster with a central tetrahedron consisting of the atoms marked A on fig. 6a, the atoms marked B are situated above the centers of the faces of the central tetrahedron. The cluster deforms in the support's field, and we have a polyhedron intermediate between a tetragonal antiprism and a dodecahedron (fig. 6b).

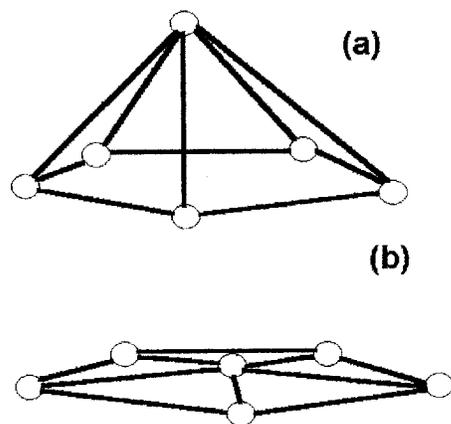


Figure 5. 6-atom case. Pentagonal bipyramid with a plane of the base parallel to the support's surface.

$\text{Ag}_{12}$ - $\text{Ag}_{13}$ . The most stable structure is icosahedron. In the case of the interaction with the support a deformation of an icosahedron and cubo-octahedron is in general similar to the deformation of the small  $\text{Ag}_5$ - $\text{Ag}_6$  clusters, a distance between the atoms of the upper layer and the atoms of the middle layer is clearly larger than a distance between lower and middle layers. When we have an atom in the center of the polyhedron a deformation is clearly less (fig. 7b).

Quite interesting is a comparison of the cluster configurations on fig. 8a and 8b. It turns out that without the interaction with the support an apical atom of the 13-atom cluster is not drawn in the hexagonal antiprism and even is not in the plane of one of the faces. Moreover, although the interaction with the surface pulls the apical atom into the plane of the hexagonal face, it nevertheless does not expand this hexagon in comparison with the opposite one. That means that that the atoms do not behave like hard spheres.

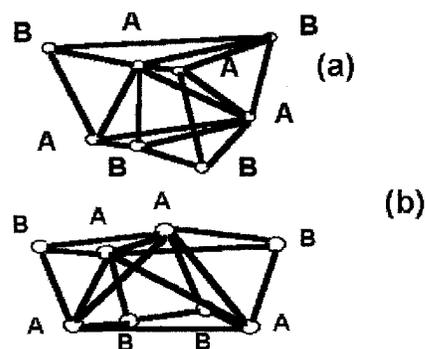


Figure 6. 8-atom case.

## Conclusions

We can see that the interaction with the support essentially changes the initial structure of the silver clusters. The influence is especially strong for small clusters, it can

change the structure completely with the tendency to put the atoms into one plane. This tendency subsists for the clusters with larger number of atoms, but the bigger is the number of atoms, the more stable is the initial structure of the cluster, and the interaction with the support only partially deforms it. The atom situated in the center of the polyhedron stabilizes the structure. We can suggest that using more exact approximations we will have the same tendency and the clusters with large number of atoms will be more structurally stable.

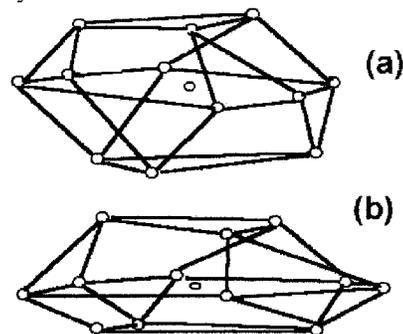


Figure 7. 13-atom case. Cubo-octahedron with a central atom.

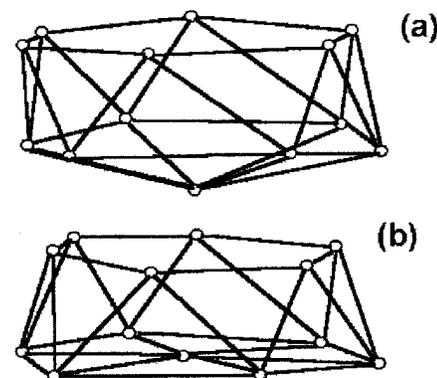


Figure 8. 13-atom case. Hexagonal antiprism.

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