Empirical many-body potential energy function for silver and gold: application to microclusters

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A recently developed empirical many-body potential energy function (PEF) has been modified and parametrized for the elements silver and gold. The PEF comprises two- and three-body atomic interactions, which satisfy both the bulk cohesive energy per atom and the bulk stability exactly, and give the bulk modulus reasonably well. The structural stability and energetics of microclusters of these elements containing three to seven atoms have been investigated. It has been found that the triangular form of trimers and the three-dimensional configurations of four- to seven-atom microclusters are energetically more stable. The present cluster configurations are qualitatively in agreement with the available literature values.

1. Introduction

Several empirical potential energy functions incorporating two- and three-body interactions have been proposed and applied to various systems in the last decade [1–4]. Recently we have proposed a new empirical many-body potential energy function (PEF) [5] (herein after I) and applied it to investigate the structural properties of three- and four-atom microclusters of elements in various crystalline structures. The PEF comprises two- and three-body atomic interactions. Here, we have modified the PEF in I and parametrized if for the elements Ag and Au in fcc structure; we then investigated the structural stability and energetics of microclusters of these elements containing three to seven atoms.

2. The potential energy function

The total interaction energy of a system of N atoms, in general, may be expressed as a many-body expansion

$$\Phi = \phi_2 + \phi_3 + \dots + \phi_n + \dots , \qquad (1)$$

where ϕ_2, ϕ_3, and ϕ_n represent the total two-body, three-body, and n-body interaction energies, respectively. One can express these multiple-body terms in terms of the positions of the atoms in the system, as follows:

$$\phi_2 = \sum_{i<j} U_{ij} , \qquad (2)$$

$$\phi_3 = \sum_{i<j<k} W_{ijk} , \qquad (3)$$

and so on. We expressed the two- and three-body interactions in I, respectively, as

$$U_{ij} = A\{(r_0/r_{ij})^{2n} \exp[-2\alpha(r_{ij}/r_0)^2] - (r_0/r_{ij})^n \exp[-\alpha(r_{ij}/r_0)^2]\} \qquad (4)$$

and

$$W_{ijk} = U_{ij}f_{ijk} + U_{ik}f_{ikj} + U_{jk}f_{jki} , \qquad (5)$$

where

$$f_{ijk} = \exp[-(r_{ik}^2 + r_{jk}^2)/r_0^2] ; \qquad (6)$$

similarly f_{ikj} and f_{jki} have the same form as f_{ijk} with suitable indices; r_{ij} is the interatomic distance between atoms i and j. The parameters A, α, n of the pair potential are expressed analytically in terms of the equilibrium distance (r_0), equilibrium energy (ϵ_0) and force constant at equilibrium (k) of the dimer:

$$A = -4\epsilon_0, \quad \alpha = \ln 2, \quad n = \sqrt{r_0^2 k/2|\epsilon_0|} - 2\alpha . \qquad (7)$$

The total interaction energy of a system was defined in I as

$$\Phi = \phi_2 + B\phi_3 , \qquad (8)$$

where B is the three-body parameter, which can be determined by equating the total interaction energy of a single atom in the bulk to the bulk cohesive energy per atom at a certain crystalline structure.

In this paper we reexpressed the total interaction energy of a system as

$$\Phi = C_2\phi_2 + C_3\phi_3 , \qquad (9)$$

where C_2 and C_3 are parameters to be determined. If one considers the bulk stability condition, at $T=0$ K ($\partial\Phi/\partial V=0$), we may write the similar expression to eq. (9) as

$$0 = C_2\phi'_2 + C_3\phi'_3 ; \qquad (10)$$

here, the prime denotes the first derivative with respect to volume. One can easily calculate C_2 and C_3 considering eqs. (9) and (10). In eq. (9), the left-

hand side is taken as the bulk cohesive energy per atom. The lattice sums ϕ_2, ϕ_3, ϕ'_2 and ϕ'_3 can be calculated from the corresponding lattice constructed for the particular element considered. In this modified form, the PEF satisfies both the bulk cohesive energy and bulk stability condition exactly.

3. Microclusters

The new PEF has been applied to investigate the structural stability and energetics of three- to seven-atom microclusters of the elements Ag and Au in fcc crystalline structure. Before cluster calculation, we tested the PEFs for the bulk structural stability. The total interaction energy per atom versus atomic volume in different crystalline structures is shown in figs. 1 and 2 for Ag and Au, respectively. The PEFs give the most stable fcc structure for both elements.

The parameters used in the calculations are given in table 1. The calculated potential parameters are
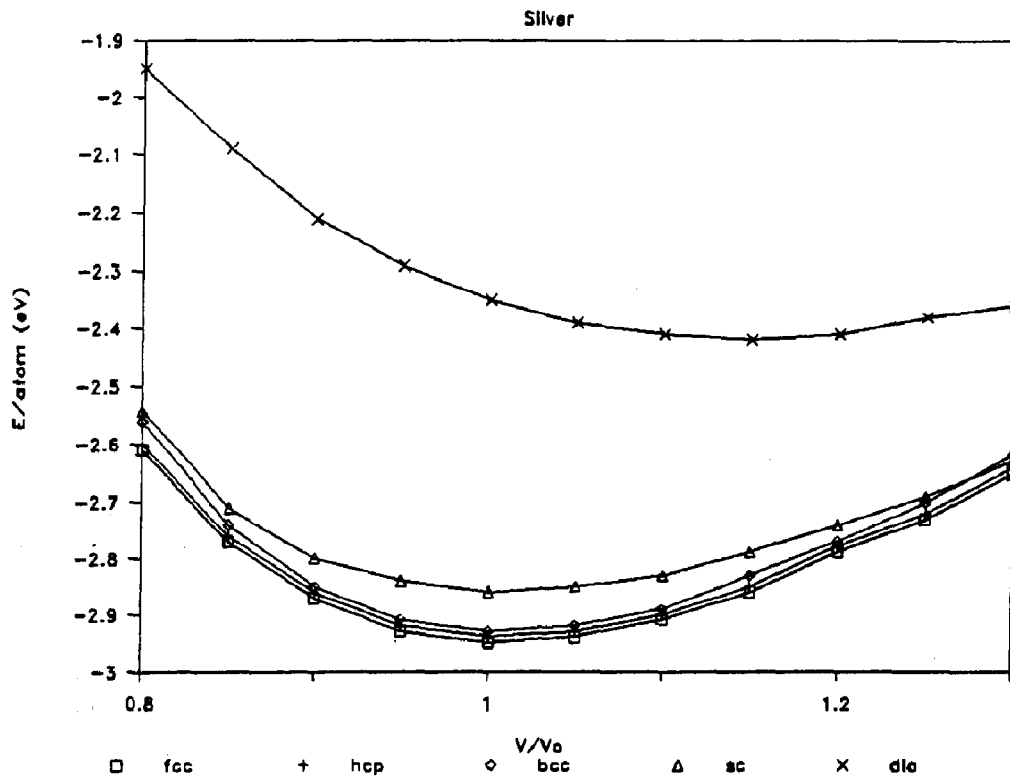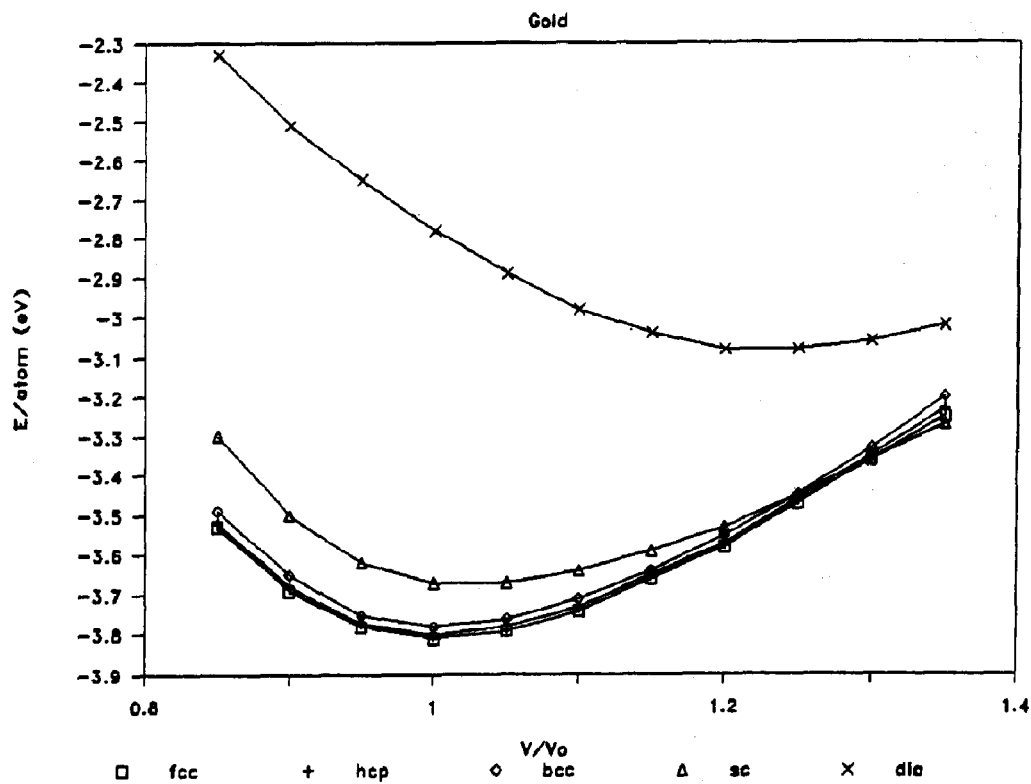

Fig. 1. Variation of bulk cohesive energy per atom versus atomic volume of Ag for various crystalline structures. V_0 is the experimental atomic volume in fcc structure; $V_0 = 17.068$ Å³.

Fig. 2. Same as fig. 1 but for Au, $V_0 = 16.891$ Å^3.

Table 1
Parameters used in the calculations

Element	r_0 (Å) [6]	$-\epsilon_0$ (eV) [6]	k (eV/Å^2) [6]	d_{nn} (Å) [7]	$-\Phi$ (eV) [7]
Ag	2.48	1.65	7.34	2.89	2.95
Au	2.47	2.29	13.20	2.88	3.81

Table 2
Calculated potential parameters and bulk modulus. $\alpha = \ln 2$ for both elements

Element	A (eV)	n	C_2	$-C_3$	B_m (eV/Å^3) cal.	exp. [6]
Ag	6.60	2.31235142	0.2338381	0.1640650	0.62	0.68
Au	9.16	2.80695973	0.2459298	0.1768174	0.96	1.13

given in table 2. The three-body parameter (C_3) has a negative value for both elements; this means that the three-body interaction has a positive contribution to the total energy. In the calculation of the potential parameters C_2 and C_3, the lattice sums have been calculated for a predetermined cut-off radius of $4.5d_{nn}$, which gives seven-digit accuracy in the parameters, where d_{nn} is the nearest-neighbour distance in the lattice.

The bulk modulus of Ag and Au have also been calculated from the relation $B_m = V \partial^2 \Phi / \partial V^2$. Calculated bulk-modulus values are given in table 2 and compared with the experimental values extrapolated to $T = 0$ K [8]. The present PEFs give bulk-modulus values 1% and 18% smaller than the corresponding
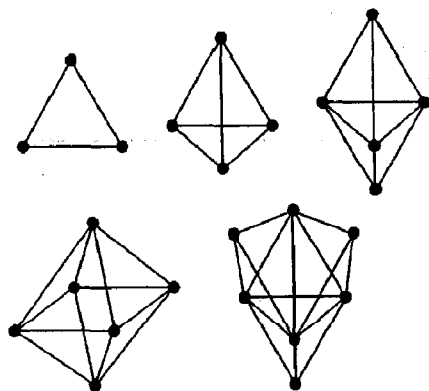

Fig. 3. Energetically the most stable structures of both Ag_n and Au_n microclusters. All the nearest-neighbour atom distances have the same value in a cluster.

experimental values for Ag and Au, respectively. For silver, the agreement between the calculated and experimental values is very good; for gold, however, it can be considered as reasonable.

In cluster applications, the total energy of the cluster has been calculated for a given geometry. We minimized the total energy by varying the interatomic distances. Various cluster models have been considered for each group, and the most energetically stable structures were selected. The most stable cluster structures are shown in fig. 3. The corresponding interatomic distances and energies are given in table 3. The variation of average interaction energy per atom versus the cluster size, namely the number of atoms in the cluster, is shown in fig. 4, which shows an expected trend. The contribution of three-body interaction energy in a cluster increases as the cluster size increases. The variation of the ratio of two- to three-body interaction energy versus the cluster size is shown in fig. 5.

The comparision of the present results with the literature values is as follows:

Ag_n. The triangular configuration of Ag_3 was found to be more stable [6]. Basch [9] in his ab initio calculation found that the ground-state energies of the linear and trigonal configurations of Ag_3 are very close to each other, but he did not optimize the interatomic distances – a fixed value of 2.778 Å was chosen. The planar and three-dimensional forms of Ag_4 are energetically almost degenerate [6,10]. The DIM method [10] gives the energy of the three-di-

Table 3
Calculated interatomic distances, a (in Å) and cluster energies (in eV) of the most stable microclusters. E_2 and E_3 are the two- and three-body contributions, respectively, to the total cluster energy, $E_T = E_2 + E_3$. E_b is the average interaction energy per atom in the cluster, $E_b = E_T / n$

Cluster	a	$-E_2$	E_3	$-E_T$	$-E_b$	$|E_2/E_3|$
Ag_3	2.518750	1.153862	0.102875	1.050987	0.350329	11.2298
Ag_4	2.568750	2.279697	0.374231	1.905466	0.476367	6.0917
Ag_5	2.590625	3.450350	0.669056	2.781294	0.556259	5.1570
Ag_6	2.603125	4.869167	1.043177	3.825990	0.637665	4.4975
Ag_7	2.575000	5.892997	1.326396	4.566602	0.652372	4.4429
Au_3	2.500000	1.685388	0.156170	1.529218	0.509739	10.7920
Au_4	2.543750	3.332704	0.574524	2.758180	0.689545	5.8008
Au_5	2.562500	5.030726	1.030274	4.000452	0.800091	4.8829
Au_6	2.571875	7.059018	1.604479	5.454539	0.909090	4.3996
Au_7	2.546875	8.522397	2.033625	6.488772	0.926967	4.1907

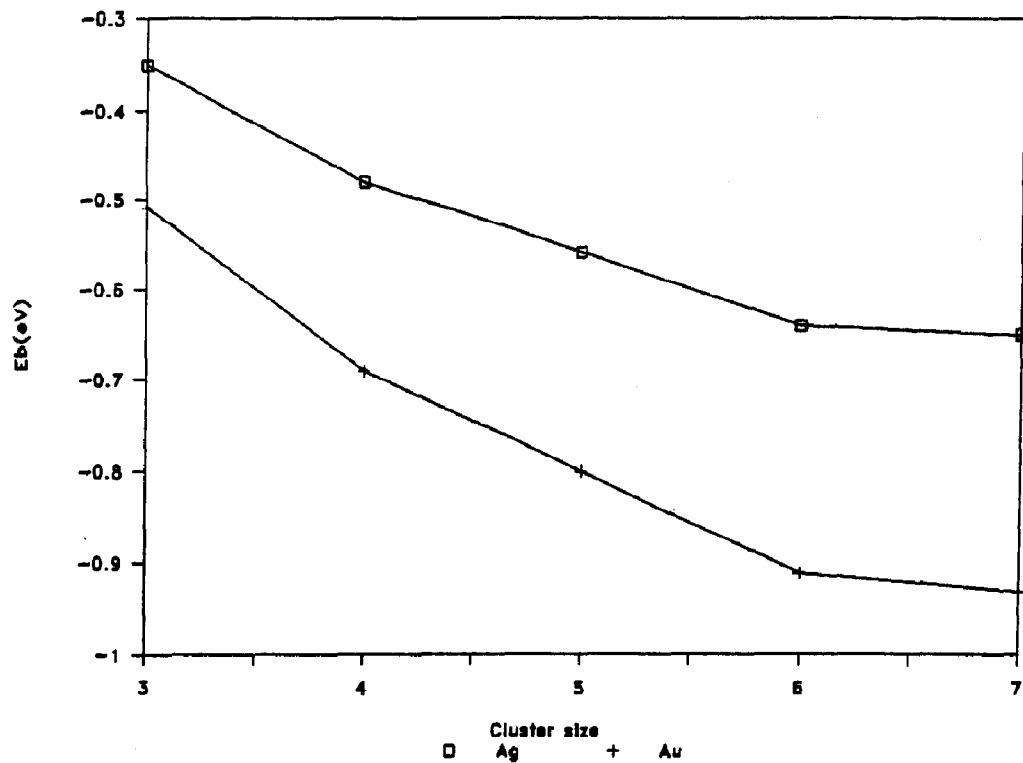Fig. 4. Variation of average total interaction energy per atom in the microclusters versus cluster size, (□): Ag; (+): Au.
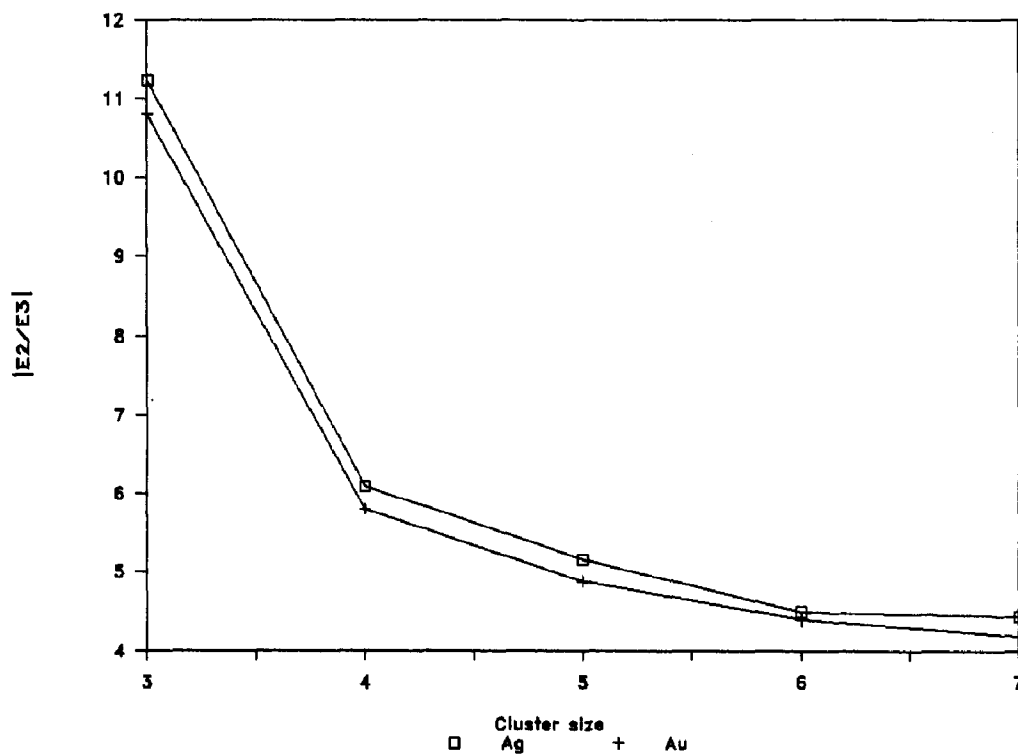

Fig. 5. Variation of the ratio of two- to three-body interaction energy in the microclusters versus cluster size, (□): Ag; (+): Au.

mensional form (trigonal pyramidal) slightly lower than that of the two-dimensional form (square). For Ag_5 clusters, experimental observation [11] and theoretical calculations [10,12] both predicted the trigonal-bipyramidal structure as most stable. For Ag_6, the DIM method [10] gives the square bipyramidal form as most stable.

Au_n. The triangular form of Au_3 was reported to be more stable [6]. With use of a Lennard-Jones and Axilrod–Teller-type empirical PEF in a molecular dynamics simulation calculation, the tetragonal form of Au_4 was calculated as most stable [13]. The DIM method [10] gives the trigonal pyramidal, trigonal bipyramidal, and square bipyramidal forms of Au_4, Au_5, and Au_6 clusters as most stable, respectively.

The general trend is that the triangular form in three-atom clusters, and the three-dimensional configuration in four- to seven-atom clusters are energetically more stable. In the previous calculations (in I), the trigonal form of trimers and the tetragonal form of tetramers of the same elements were found to be more stable. In the present calculation, energetically the most stable structures of three-atom clusters are in triangular form, the four-atom clusters are in tetragonal form, the five-atom clusters are in trigonal-bipyramidal form, the six-atom clusters are in square-bipyramidal form, and finally the seven-atom clusters are in a configuration such that three tetragonals are connected to three faces of a third tetragon, which forms a three-dimensional compact structure. The present results are qualitatively in good agreement with the available literature values.

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