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A New Class of Empirical Many-Body Potential Energy Functions for Bulk and Cluster Properties

Application to F.C.C. Metals

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A new empirical many-body potential energy function (PEF) is proposed, which comprices two- and three-body atomic interactions. The two-body potential is a kind of hybrid function and the three-body potential is formed by additive and nonadditive functions. The additive part is expressed in terms of two-body interactions, and the nonadditive part is expressed as triple-dipole function. The PEF satisfies bulk cohesive energy, bulk stability condition, and bulk modulus. The PEF is parameterized for gold, silver, and copper elements in f.c.c. crystal structure. The elastic constants of the elements are calculated, and the structural stability and energetics of microclusters containing 3 to 7 atoms of the same elements are investigated. The calculated elastic constants are in good agreement with experimental values, and the most stable microcluster geometries are qualitatively in agreement with the available literature data.

Eine neue empirische Vielteilchen-Potential-Energie-Funktion (PEF) wird vorgeschlagen, die atomare Zwei- und Drei-Körperwechselwirkungen enthält. Das Zweikörperpotential ist eine Art von Hybridfunktion und das Dreikörperpotential wird durch additive und nichtadditive Funktionen gebildet. Der additive Teil wird mit Zweikörperwechselwirkungen ausgedrückt, und der nichtadditive Teil als Tripel-Dipolfunktion. Die PEF genügt der Volumenkohäsionsenergie, der Volumenstabilitätsbedingung und dem Elastizitätsmodul. Die PEF wird für Gold, Silber und Kupfer in k.f.z. Kristallstruktur parametrisiert. Die elastischen Konstanten der Elemente werden berechnet und die Strukturstabilität und -energie der 3 bis 7 Atome enthaltenen Mikrocluster derselben Elemente untersucht. Die berechneten elastischen Konstanten sind in guter Übereinstimmung mit experimentellen Werten und die stabilsten Mikroclustergeometrien sind mit Literaturdaten qualitativ in Übereinstimmung.

1. Introduction

Computer simulations using empirical potential energy functions have been used successfully to investigate various properties such as bulk, surface, and clusters of elements at the atomistic level. Many of these simulations are based on empirical model potentials describing interactions among the atoms in the system. Several empirical potential energy functions incorporating two- and three-body interactions have been proposed and applied to various systems in the last decade [1 to 6].

Here we propose a new class of empirical many-body potential energy function (PEF), which appears to be suitable for bulk and cluster properties for different systems in different structures. As an application the proposed PEF has been parameterized for the f.c.c. metal elements gold, silver, and copper. The elastic constants of these elements have been calculated, and stability and energetics of three- to seven-atom microclusters of the same elements have been investigated.

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2. The Potential Energy Function

Total interaction energy of a system of N atoms, in general, may be expressed as a many-body expansion [7],

$$\Phi = \varphi_2 + \varphi_3 + \dots + \varphi_n + \dots , \tag{1}$$

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 multi-body terms in terms of the positions of the atoms in the system. Here we define the total interaction energy of a system in terms of two-body and three-body interactions only. In the previously proposed PEFs researchers usually expressed the three-body part either as an additive function or as a nonadditive function. Here we expressed the three-body function as the combination of an additive and a nonadditive function. The additive function is expressed in terms of two-body interactions, same was proposed recently [6]. The nonadditive function is expressed as a triple-dipole function, same as the Axilrod-Teller function [8].

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

$$\Phi = C_2\varphi_2 + C_{31}\varphi_{31} + C_{32}\varphi_{32} , \tag{2}$$

where φ_2, φ_{31}, and φ_{32} are the total two-body, additive three-body, and nonadditive three-body interaction energies, respectively,

$$\varphi_2 = \sum_{i<j} U_{ij} , \tag{3}$$

$$\varphi_{31} = \sum_{i<j<k} W_{ijk}^{(1)} , \tag{4}$$

$$\varphi_{32} = \sum_{i<j<k} W_{ijk}^{(2)} . \tag{5}$$

We define the two-body (U_{ij}), the additive three-body ($W_{ijk}^{(1)}$), and the nonadditive three-body ($W_{ijk}^{(2)}$) atomic interactions in terms of interatomic distances as

$$U_{ij} = A_1 r_{ij}^{-\lambda_1} e^{-x_1 r_{ij}^2} - A_2 r_{ij}^{-\lambda_2} e^{-x_2 r_{ij}^2} , \tag{6}$$

$$W_{ijk}^{(1)} = U_{ij} f_k + U_{ik} f_j + U_{jk} f_i , \tag{7}$$

$$W_{ijk}^{(2)} = \frac{1 + 3 \cos\theta_i \cos\theta_j \cos\theta_k}{(r_{ij} r_{ik} r_{jk})^3} , \tag{8}$$

where

$$f_i = e^{-g_i} , \qquad f_j = e^{-g_j} , \qquad f_k = e^{-g_k} , \tag{9}$$

and

$$g_i = \frac{r_{ij}^2 + r_{ik}^2}{r_0^2} ,$$

$$g_j = \frac{r_{ij}^2 + r_{jk}^2}{r_0^2} , \tag{10}$$

$$g_k = \frac{r_{ik}^2 + r_{jk}^2}{r_0^2} .$$

Table 1

Two-body potential parameters for Au, Ag, and Cu (energy in eV, distance in 10^{-1} nm)

parameter	Au	Ag	Cu
A_1	345.923364	220.262366	110.766008
A_2	38.9245908	26.0811795	46.1649783
α_1	0.750775965	0.673011507	0.394142248
α_2	0.229377368	0.120620395	0.207225507
λ_1	1.04289230	1.72376253	2.09045946
λ_2	1.05974062	1.81484791	1.49853083
r_0	2.470	2.480	2.220

Here r_{ij} is the interatomic distance between atoms i and j, and θ_i, θ_j, and θ_k are the angles of the triangle formed by the three atoms i, j, and k. r_0 is the equilibrium distance of the pair potential, where the pair energy is minimum. C_2, C_{31}, and C_{32} are the parameters to be determined.

The present pair potential (6) contains six parameters, three parameters in the repulsive part $(A_1, \lambda_1, \alpha_1)$, and three parameters in the attractive part $(A_2, \lambda_2, \alpha_2)$. These parameters are determined by fitting the pair function to the experimentally determined curve, which are taken from [9] for the elements considered in this work. Calculated pair potential parameters are given in Table 1. The fit is perfect, the pair function fits to the exact curve at every part. The fitting procedure has been performed by the nonlinear least-squares method.

Considering the bulk stability condition, at $T = 0$ K, $(\partial \Phi / \partial V = 0)$, we may write

$$0 = C_2 \varphi'_2 + C_{31} \varphi'_{31} + C_{32} \varphi'_{32}, \tag{11}$$

where the prime denotes the first derivative with respect to volume, V. Similarly considering the bulk modulus of a solid, $B_m = V(\partial^2 \Phi / \partial V^2)$, we may write

$$9VB_m = C_2 \varphi''_2 + C_{31} \varphi''_{31} + C_{32} \varphi''_{32}, \tag{12}$$

where the double prime denotes the second derivative with respect to volume. One can easily calculate C_2, C_{31}, and C_{32} considering (2), (11), and (12). In (2) the left-hand side is taken as bulk cohesive energy per atom. In (12) V is the atomic volume in the crystal, and B_m is the bulk modulus of the element considered. The lattice sums φ_2, φ_{31}, φ_{32}, φ'_2, φ'_{31}, φ'_{32}, φ''_2, φ''_{31}, and φ''_{32} can be calculated from the corresponding lattice constructed for a particular element considered. Therefore, the PEF satisfies the bulk cohesive energy, the bulk stability condition, and the bulk modulus exactly.

3. Bulk Properties

The bulk parameters used in the calculations are given in Table 2. The calculated potential parameters are given in Table 3. In the calculation of potential parameters C_2, C_{31}, and C_{32}, the lattice sums have been calculated for a predetermined cut-off radius of $4.5d_{nn}$, which gives at least seven-digit accuracy in the parameters, where d_{nn} is the nearest-neighbor distance in the lattice. The calculated parameters C_2, C_{31}, and C_{32} are positive for the elements considered. The contribution of each term in (2) in the bulk is given in Table 4. The additive three-body interaction is negative, however, the nonadditive three-body interaction is positive for all the elements considered. The total three-body contribution for gold is negative, but for silver and copper positive.

Table 2

Bulk parameters used in the calculations

element	d_{nn} $(10^{-1}$ nm) [18]	$-\Phi$ (eV) [18]	B_m $(10^3$ eV/nm$^3)$ [11]
Au	2.88	3.81	1.13
Ag	2.89	2.95	0.68
Cu	2.56	3.49	0.89

Table 3

Calculated parameters for the PEF

element	C_2	C_{31}	C_{32}
Au	0.169729418	0.530820957	1487.33142
Ag	0.193714755	0.254330241	784.190491
Cu	0.150036137	0.140549073	194.576839

Table 4

Calculated energy contributions (in eV) in the bulk. E_2, E_{31}, and E_{32} are the total two-body, additive three-body, and nonadditive three-body contributions, respectively, to the total interaction energy per atom (cohesive energy) in the bulk

element	$-E_2$	$-E_{31}$	E_{32}	E_3	$-E_T$
Au	3.696298796	6.349134551	6.235433348	−0.113701203	3.810
Ag	3.639878723	2.496755853	3.186634581	0.689878728	2.950
Cu	3.818393745	2.026236575	2.354630328	0.328393753	3.490

$$E_3 = E_{31} + E_{32}, \quad E_T = E_2 + E_3$$

The present PEF also satisfies the stability criterion: cohesive energy per atom in different crystalline structures. Among the structures f.c.c., h.c.p., b.c.c., dia, and s.c., the f.c.c. structure has found to be energetically most stable, the cohesive energy per atom in these structures for gold is shown in Fig. 1.
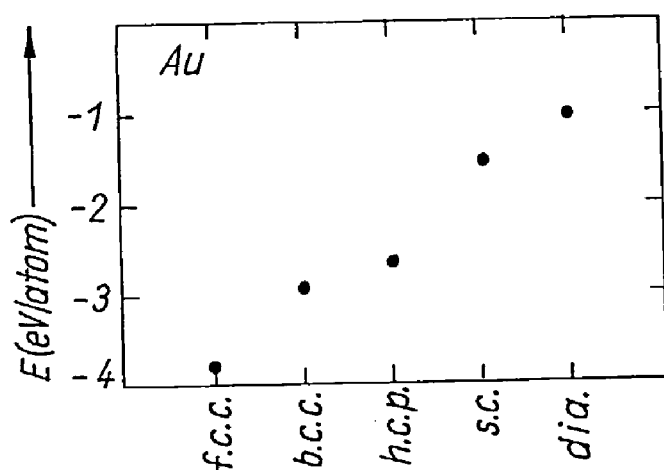

Fig. 1. Cohesive energy per atom for Au in different crystalline structures

Table 5

Calculated elastic constants (in 10^3 eV/nm^3). Values in parantheses are experimentally predicted at $T = 0$ K [11]

element	C_{11}	C_{12}	C_{44}	$(C_{11} + 2C_{12})/3$
Au	1.398	0.996	0.271	1.130
	(1.26)	(1.06)	(0.28)	(1.13)
Ag	0.868	0.586	0.163	0.680
	(0.82)	(0.61)	(0.32)	(0.68)
Cu	1.104	0.783	0.232	0.890
	(1.10)	(0.78)	(0.51)	(0.89)

The parameterized PEF is used to calculate the elastic constants of the elements considered. We calculated the elastic constants at $T = 0$ K from the general expression [10]

$$C_{\alpha\beta\gamma\delta} = \frac{1}{V}\left(\frac{\partial^2 \Phi}{\partial \eta_{\alpha\beta}\, \partial \eta_{\gamma\delta}}\right). \tag{13}$$

The calculated elastic constants are given in Table 5 and compared with the experimental values extrapolated to $T = 0$ K [11]. The calculated elastic constants satisfy the conditions for mechanical stability in cubic systems, $C_{11} > C_{12} > C_{44} > 0$, and $B_m = (C_{11} + 2C_{12})/3$. The agreement between calculated and experimentally predicted values is good.

4. Microclusters

The new PEF has been applied to investigate the structural stability and energetics of three- to seven-atom microclusters of the elements considered. The total energy of the cluster has been calculated for a given geometry. We minimized the energy by varying the interatomic distances. Various cluster models have been considered for each group and energetically the most stable structures were selected. The most stable cluster structures are shown in Fig. 2. The corresponding interatomic distances and energies are given in
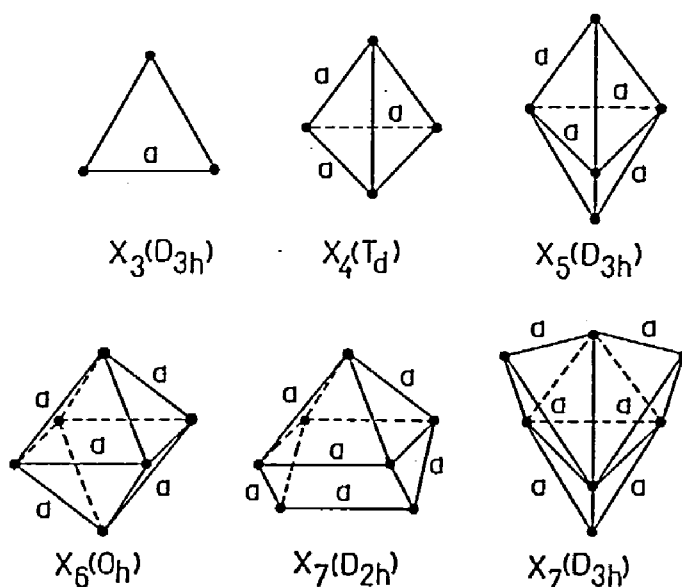

$X_3(D_{3h})$　　　　$X_4(T_d)$　　　　$X_5(D_{3h})$

$X_6(O_h)$　　　　$X_7(D_{2h})$　　　　$X_7(D_{3h})$

Fig. 2. Energetically the most stable microcluster structures. All the nearest-neighbor atom distances have the same value in a cluster

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Table 6

Calculated interatomic distances, a (in 10^{-1} nm) and cluster energies (in eV) of the most stable microclusters. E_2, E_{31}, and E_{32} are the total two-body, additive three-body, and nonadditive three-body energy contributions, respectively, to the total cluster energy

cluster	a	$-E_2$	$-E_{31}$	E_{32}	E_3	$-E_T$	$-E_b$
$Au_3(D_{3h})$	2.5687500	1.1408	0.4102	0.4200	0.0098	1.1310	0.3770
$Au_4(T_d)$	2.6125000	2.2239	1.4847	1.4430	-0.0417	2.2657	0.5664
$Au_5(D_{3h})$	2.6093750	3.3648	2.7562	2.6135	-0.1427	3.5075	0.7015
$Au_6(O_h)$	2.5890625	4.7426	4.4999	4.3370	-0.1629	4.9055	0.8176
$Au_7(D_{3h})$	2.5718750	5.6774	5.6365	5.2559	-0.3806	6.0580	0.8654
$Ag_3(D_{3h})$	2.5812500	0.9321	0.1402	0.2120	0.0718	0.8603	0.2868
$Ag_4(T_d)$	2.6500000	1.7936	0.4800	0.6692	0.1892	1.6044	0.4011
$Ag_5(D_{3h})$	2.6531250	2.7217	0.8838	1.1864	0.3026	2.4190	0.4838
$Ag_6(O_h)$	2.6406250	3.8654	1.4370	1.9148	0.4778	3.3875	0.5646
$Ag_7(D_{3h})$	2.6187500	4.6603	1.8117	2.3554	0.5437	4.1167	0.5881
$Cu_3(D_{3h})$	2.3250000	0.8995	0.0940	0.1348	0.0408	0.8587	0.2862
$Cu_4(T_d)$	2.3812500	1.7574	0.3297	0.4347	0.1050	1.6524	0.4131
$Cu_5(D_{3h})$	2.3812500	2.6730	0.6117	0.7789	0.1672	2.5058	0.5012
$Cu_6(O_h)$	2.3562500	3.8474	1.0418	1.3248	0.2830	3.5644	0.5941
$Cu_7(D_{2h})$	2.2968750	4.6853	1.2493	1.6190	0.3697	4.3155	0.6165

$E_3 = E_{31} + E_{32}$, $E_T = E_2 + E_3$. E_b is the average interaction energy per atom in the cluster, $E_b = E_T/N$

Table 6. The variation of average interaction energy per atom versus the cluster size, namely the number of atoms in the cluster, is shown in Fig. 3, which shows an expected trend. Same as the bulk properties, the total three-body energy is negative for gold clusters, except Au_3, and positive for silver and copper clusters.

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

Au_n: The triangular form of Au_3 was reported to be more stable [9]. The DIM method [12] gives the trigonal pyramidal, trigonal bipyramidal, and square bipyramidal forms of Au_4, Au_5, and Au_6 clusters as most stable, respectively. In a recent calculation considering a different PEF [6b], we obtained the same structures as the present calculations.
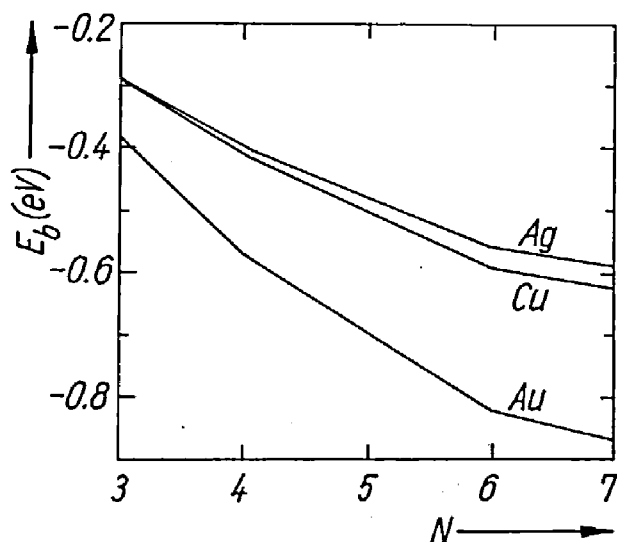

Fig. 3. Variation of average total interaction energy per atom in the most stable microclusters vs. cluster size

Ag_n: The triangular configuration of Ag_3 was found to be more stable [9]. Basch [13] 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 0.2778 nm was chosen. The planar and three-dimensional forms of Ag_4 are energetically almost degenerate [9, 12]. The DIM method [12] gives the energy of the three-dimensional form (trigonal pyramidal) slightly lower than that of the two-dimensional form (square). For Ag_5 clusters experimental observation [14] and theoretical calculations [12, 15] both predicted the trigonal-bipyramidal structure as most stable. For Ag_6, the DIM method [12] gives the square bipyramidal form as most stable. Our previous calculation [6b] gives the same structures as the present results.

Cu_n: The triangular form of Cu_3 and the tetragonal form of Cu_4 clusters were found to be more stable [16]. For Cu_5 both experimental observation [16] and ab-initio calculation [15] predicted the trigonal-bipyramidal structure as most stable. The square-bipyramidal form of Cu_6 was calculated [17] as most stable. Our previous calculation [6 b] gives the same structures as the present results, but the Cu_7 structure is different from the previous calculation; it had the pentagonal-bipyramidal structure.

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 present calculation, energetically the most stable structures of three-atom clusters are in trigonal form with D_{3h} symmetry for all the elements considered, the four-atom clusters are in tetragonal form with T_d symmetry for all three elements, the five-atom clusters are in trigonal-bipyramidal form with D_{3h} symmetry for all three elements, the six-atom clusters are in square-bipyramidal form with O_h symmetry again for all three elements, and finally the seven-atom clusters are in a configuration such that three tetragonals are connected to three faces of a fourth tetragon with D_{3h} symmetry for Au_7 and Ag_7, which forms a three-dimensional compact structure, however, Cu_7 is square-pyramidal having two atoms underneath with D_{2h} symmetry. The energy of $Ag_7(D_{2h})$ and $Ag_7(D_{3h})$ are very close to each other but it is slightly lower for $Ag_7(D_{3h})$.

The interatomic distances (a) in the most stable microclusters of all the elements considered are relatively larger than the corresponding equilibrium distance (r_0) of their dimers, and relatively smaller than the corresponding nearest-neighbor distance (d_{nn}) of their bulk values, namely $(r_0 < a < d_{nn})$, as expected. The present results are qualitatively in good agreement with the available literature values.

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