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A New Empirical Many-Body Potential Energy Function

Application to Microclusters

By

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A new empirical many-body potential energy function is proposed which comprises two- and three-body interactions. The two-body potential is a kind of hybrid function and the three-body potential is expressed in terms of the two-body interactions. The parameters of the potential energy function can be easily evaluated using dimer data and the bulk cohesive energy of the system considered. The proposed potential energy function is parameterized for several elements in f.c.c., b.c.c., and diamond structures and is applied for the investigation of structural stability and energetics of microclusters. The agreement between the present results and literature values is good.

Eine neue empirische Viel-Körper-Potentialfunktion wird vorgeschlagen, die Zwei- und Dreikörperwechselwirkungen beschreibt. Das Zwei-Körperpotential ist eine Art von Hybridfunktion und das Drei-Körper-Potential wird durch Zwei-Körperwechselwirkungen ausgedrückt. Die Parameter der Potentialenergiefunktion können mit Dimerdaten und der Volumenkohäsionsenergie des betrachteten Systems einfach berechnet werden. Die vorgeschlagene Potentialfunktion wird für einige Elemente in k.f.z., k.r.z.- und Diamant-Strukturen parametrisiert und zur Untersuchung der Strukturstabilität und Energetik von Mikroclustern angewendet. Die Übereinstimmung zwischen den vorgelegten Ergebnissen und Literaturwerten ist gut.

1. Introduction

There has been growing interest in the structural properties and energetics of various systems in the last decade. 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. This paper proposes a new empirical potential energy function (PEF) which is easy to parameterize and applicable to different structures.

The model potentials are usually expressed as a many-body expansion of the total PEF of the system. If it is assumed that in the absence of external forces a function $\Phi(r_1, r_2, \dots, r_N)$ exists to describe the total potential energy of a system of N atoms as a function of their positions, it can be resolved into two-body, three-body, etc., contributions as follows [1]:

$$\Phi(r_1, r_2, \dots, r_N) = \sum_{i < j} U(r_i, r_j) + \sum_{i < j < k} W(r_i, r_j, r_k) + \dots \quad (1)$$

It is usually believed that this series is rapidly convergent and that the first two terms (two- and three-body contributions only) give a reasonable approximation to the interaction potential, therefore, the higher moments may be neglected [2, 3]. In the

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early applications, the expansion has been truncated after the two-body term. However, it has been shown that the three-body term makes important contributions to the structure and to the stability of different microclusters [4], and is essential for an understanding of the surface multilayer relaxation in crystals [5].

Recently, several empirical PEFs incorporating two- and three-body interactions have been proposed and applied to various bulk, surface, and small cluster properties of covalently bonded systems, particularly to silicon, by Pearson et al. [6], Stillinger and Weber [7], and Tersoff [8]. These potentials include, respectively, three, nine, and eleven parameters to be evaluated for a monatomic system. A detailed comparative analysis of these potential functions has been reported recently [9]. The evaluation of parameters of a model potential function is a time consuming job. The difficulty, in general, increases with increasing number of parameters to be determined.

Here I propose a qualitatively new interatomic potential, which appears to be easier to parameterize for different systems in different structures than the conventional two- and three-body potentials.

The functional form and the parametrization procedure of the proposed PEF is explained in Section 2. As an application of the proposed PEF, the structural stability and the energetics of the microclusters of the elements considered in Section 2 have been discussed in Section 3.

2. The Potential Energy Function

The starting point is to express the total interaction energy for a system of N particles based on the formal many-body expansion (1). Only two- and three-body interactions are taken into account. In general, the realistic two-body interactions are commonly described, in the literature, by the Morse potential [10], the Mie potential [11] with different combinations of powers, the Buckingham potential [12], and the various combinations of $1/r^n$ and exponential functions [13].

Here I propose a pair potential between two interacting atoms as the combination of $1/r^{2n}$ and $1/r^n$ with the product of Gaussians $e^{-2\alpha r^2}$ and $e^{-\alpha r^2}$, respectively, both for repulsive and attractive parts. More explicitly,

$$U(r_j, r_i) = U(r_{ij}) = U_{ij} \\ = A \left[\left(\frac{r_0}{r_{ij}} \right)^{2n} e^{-2\alpha(r_{ij}/r_0)^2} - \left(\frac{r_0}{r_{ij}} \right)^n e^{-\alpha(r_{ij}/r_0)^2} \right], \quad (2)$$

where A , α , and n are the potential parameters to be evaluated. r_{ij} is the interatomic distance between the atoms i and j , $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$. The Gaussians make the $1/r$ parts more flexible to fit the dimer data. Here r_0 may be taken as the equilibrium distance of the dimer. The equilibrium distance, r_0 , the pair energy at the equilibrium, ϵ_0 , and the force constant at the equilibrium, k , can be easily determined from the experimental observations or from the accurate ab initio calculations. These parameters (r_0 , ϵ_0 , k) are available in the literature for most of the dimers. The two-body potential parameters (A , α , n) can be easily evaluated considering the relations

$$U(r_{ij})|_{r_{ij}=r_0} = \epsilon_0, \quad (3)$$

$$\left. \frac{\partial U(r_{ij})}{\partial r_{ij}} \right|_{r_{ij}=r_0} = 0, \quad (4)$$

$$\left. \frac{\partial^2 U(r_{ij})}{\partial r_{ij}^2} \right|_{r_{ij}=r_0} = k. \quad (5)$$

In terms of r_0 , ϵ_0 , and k , the two-body potential parameters are obtained analytically as

$$A = -4\epsilon_0, \quad (6)$$

$$\alpha = \ln 2, \quad (7)$$

and

$$n = \left\lceil \sqrt{\frac{r_0^2 k}{2 |\epsilon_0|}} - 2\alpha \right\rceil. \quad (8)$$

Here α turns out to be a constant. On the other hand, the powers of the $1/r$ terms are not integer. These simple relations (6) to (8) are possible only for the proposed pair potential, (2). Therefore, one can say that the present pair potential exactly fits to the dimer data, which guarantees the two-body contribution to be more accurate in the many-body expansion. Moreover, the present pair potential can be used for every homonuclear and heteronuclear diatom, provided that the parameter set (r_0 , ϵ_0 , k) is available.

In the literature, there are several three-body interaction functions [4 to 8]. In recent years, the commonly used functions have been the multiple dipole interaction functions, for example, the Axilrod-Teller-type triple-dipole function [14]. Although the Axilrod-Teller function is derived for the rare gas solids, it is successfully used in many applications for different purposes by Halicioğlu et al.

Here I propose a three-body interaction potential as the linear combination of pair energies formed by the three particles. In this combination each function is multiplied by a Gaussian-type function depending on the distances of the pair atoms to the third atom. More explicitly,

$$\begin{aligned} W(r_i, r_j, r_k) &= W(r_{ij}, r_{ik}, r_{jk}) = W_{ijk} \\ &= B(U_{ij}f_{ijk} + U_{ik}f_{ikj} + U_{jk}f_{jki}), \end{aligned} \quad (9)$$

where

$$f_{ijk} = e^{-(r_{ik}^2 + r_{jk}^2)/r_0^2}, \quad (10)$$

$$f_{ikj} = e^{-(r_{ij}^2 + r_{jk}^2)/r_0^2}, \quad (11)$$

and

$$f_{jki} = e^{-(r_{ij}^2 + r_{ik}^2)/r_0^2} \quad (12)$$

are the Gaussian factors. Here B is the only parameter, in the three-body function, to be evaluated. The potential possesses all physically required invariance properties.

The three-body potential parameter, B , can be evaluated easily by fitting the total interaction energy of an atom, in a particular crystal structure, to the bulk cohesive energy of the element. One can write the total interaction energy simply by separating B as

$$\Phi = \Phi_2 + B\Phi_3. \quad (13)$$

There is no special cut-off parameter in the present PEF. However, it is found that, in the calculation of the lattice sums in Φ_2 and Φ_3 , a cut-off radius of $4d_{nn}$ is enough to reach a seven-digit accuracy in B for all the elements considered in the present calculations. d_{nn} is the nearest-neighbor distance in the crystal structure.

The proposed empirical many-body PEF is parameterized for the following monatomic systems: Ag, Al, Au, Cu, and Ni in f.c.c. structure, Fe and Li in b.c.c. structure, and C, Ge, and Si in diamond structure. The necessary parameters used in the calculations are given in Table 1, and the calculated potential parameters are given in

Table 1
Parameters used in the calculations

element	r_0 (10^{-1} nm)	ϵ_0 (eV)	k (eV/ 10^{-2} nm ²)	d_{nn} (10^{-1} nm) [19]	ϕ (eV) [19]
Ag	2.48 [17]	-1.65 [17]	7.34 [17]	2.89	-2.95
Al	2.47 [20]	-1.55 [20]	6.08 [20]	2.86	-3.39
Au	2.47 [17]	-2.29 [17]	13.20 [17]	2.88	-3.81
Cu	2.22 [17]	-2.01 [17]	8.29 [17]	2.56	-3.49
Ni	2.20 [17]	-2.07 [17]	15.66 [17]	2.49	-4.44
Fe	2.02 [17]	-0.90 [17]	9.26 [17]	2.48	-4.28
Li	2.67 [21]	-1.07 [21]	1.58 [21]	3.02	-1.63
C	1.24 [20]	-6.21 [20]	75.97 [20]	1.54	-7.37
Ge	2.45 [22]	-2.65 [22]	6.94 [22]	2.45	-3.85
Si	2.25 [20]	-3.21 [20]	13.48 [20]	2.35	-4.63

Table 2
Calculated potential parameters. $\alpha = \ln 2$ for all the elements

element	A (eV)	n	B
Ag	9.92	2.312351	- 1.637860
Al	9.88	2.072844	- 1.553508
Au	9.88	2.806960	- 1.605480
Cu	8.88	1.801698	- 1.619242
Ni	8.80	2.892470	- 1.290433
Fe	8.08	3.195342	- 1.061661
Li	10.68	0.907914	- 1.888711
C	4.96	1.680481	- 17.293200
Ge	9.80	1.417253	- 3.344464
Si	9.00	1.874024	- 4.266564

Table 2. The three-body potential parameter, B , has a negative value for all the elements considered. This means that the three-body potential has a positive contribution to the total interaction energy.

3. Application to Microclusters

The structural study of small clusters has become a topic of considerable interest in the last five or six years, both from theoretical and experimental viewpoints [15 to 18]. Research about small clusters is particularly intense because of their relevance to surface science in general and heterogeneous catalysis in particular.

The present empirical many-body potential energy function is used, as an application, to investigate the structural stability and the energetics of microclusters of the elements parameterized in Section 2. Only the three- and four-atom clusters have been considered. For the three-atom clusters the linear and triangular geometries, in the case of four-atom clusters linear, square, rhombic, and tetrahedral geometries have been taken into account. The cluster types considered are shown in Fig. 1. The total interaction energy of the cluster is minimized by varying the interatomic distances simultaneously. The calculated optimum interatomic separations, two- and three-body energy contributions, total energy of the cluster, and the average interac-

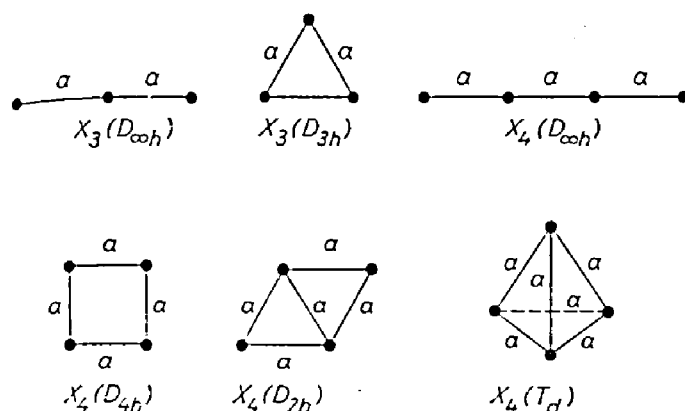


Fig. 1. Three- and four-atom micro-cluster types

tion energy per atom in the cluster are given in Table 3. The minimum contribution of the three-body part is in iron and the maximum contribution in carbon, among all the clusters considered.

The comparison of the present results with the literature values is as follows: For Ag_3 clusters [17], the triangular configuration was found to be energetically more stable than the linear form, and for Ag_4 clusters [17], it was determined that the square, rhombic, and tetrahedral forms are energetically almost degenerate. Pettersson et al. [23] reported that the triangular form of Al_3 and the rhombic configuration of Al_4 are more stable. For Au_3 clusters [17], the triangular form was reported to be more stable. In a molecular-dynamics calculation [24] using Halicioğlu et al.'s potential [25], it was found that the tetrahedral geometry is more stable. The triangular form of Cu_3 and the tetrahedron form of Cu_4 clusters were found to be more stable [16]. For Ni_3 clusters [17], the triangular form was reported to be more stable. Information about Ni_4 clusters does not exist in the literature. The general trend is that in f.c.c. metal microclusters the triangular form in three-atom clusters and the tetrahedral configuration in four-atom microclusters are energetically more stable. The present results are qualitatively in good agreement with the literature values for these elements.

The triangular form of Fe_3 and the tetrahedral form of Fe_4 were found to be more stable [16]. On the other hand, the triangular form of Li_3 and the square form of Li_4 were reported to be more stable [16]. The present Li_4 cluster energies for the square and the tetrahedral configurations are very close to each other (almost degenerate) but the tetrahedral configuration is favourable. The comparison between the present results and the literature values for the microclusters of the b.c.c. elements is also qualitatively in good agreement.

For the carbon clusters the linear configurations were found to be more stable both for C_3 and C_4 clusters [16]. The present results are in good agreement with the literature values for carbon clusters. For Ge clusters [26], the linear form in three-atom clusters and the rhombic form in four-atom clusters were calculated to be energetically more stable. However, the present results indicate that Ge_3 clusters are energetically almost degenerate, but that the triangular form is favorable, and the square form in Ge_4 clusters is calculated as more stable. For Si_3 clusters [27], the linear configuration was reported to be more stable; for Si_4 clusters [28], the square configuration was calculated to be more stable. The agreement between the present results and the literature values is qualitatively good.

As a conclusion, the proposed empirical many-body PEF works well for the microclusters of elements in different structures. Application of the present PEF to surface multilayer relaxation, to surface reconstruction, and to the elastic properties of

Table 3

Calculated cluster energies (in eV) and interatomic distances (in 10^{-1} nm). 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, $E_b = E_T/N$

X	cluster	a	$-E_2$	E_3	$-E_T$	$-E_b$
Ag	3(D _{∞h})	2.478125	3.3825	0.0550	3.3274	1.1091
	3(D _{3h})	2.587500	4.8424	0.8991	3.9433	1.3144
	4(D _{∞h})	2.478125	5.1160	0.1101	5.0058	1.2515
	4(D _{4h})	2.559375	7.6564	1.3176	6.3388	1.5847
	4(D _{2h})	2.631250	8.0696	1.8052	6.2644	1.5661
	4(T _d)	2.740625	8.8916	2.5325	6.3592	1.5898
Al	3(D _{∞h})	2.465625	3.1918	0.0525	3.1393	1.0464
	3(D _{3h})	2.584375	4.5489	0.7913	3.7576	1.2525
	4(D _{∞h})	2.462500	4.8364	0.1065	4.7300	1.1825
	4(D _{4h})	2.550000	7.2876	1.2049	6.0828	1.5207
	4(D _{2h})	2.625000	7.6205	1.6063	6.0141	1.5034
	4(T _d)	2.737500	8.4049	2.2385	6.1664	1.5416
Au	3(D _{∞h})	2.471875	4.6605	0.0666	4.5939	1.5313
	3(D _{3h})	2.553125	6.7522	1.2794	5.4728	1.8243
	4(D _{∞h})	2.471875	7.0319	0.1333	6.8986	1.7246
	4(D _{4h})	2.528125	10.4722	1.8084	8.6637	2.1659
	4(D _{2h})	2.590625	11.2336	2.5965	8.6371	2.1593
	4(T _d)	2.684375	12.4890	3.7780	8.7110	2.1778
Cu	3(D _{∞h})	2.212500	4.1646	0.0776	4.0870	1.3623
	3(D _{3h})	2.343750	5.8711	1.0231	4.8480	1.6160
	4(D _{∞h})	2.212500	6.3216	0.1552	6.1664	1.5416
	4(D _{4h})	2.309375	9.5141	1.5900	7.9242	1.9810
	4(D _{2h})	2.384375	9.8403	2.0566	7.7837	1.9459
	4(T _d)	2.496875	10.7735	2.7793	7.9942	1.9985
Ni	3(D _{∞h})	2.200000	4.2091	0.0481	4.1610	1.3870
	3(D _{3h})	2.253125	6.1506	0.9741	5.1765	1.7255
	4(D _{∞h})	2.200000	6.3489	0.0962	6.2527	1.5632
	4(D _{4h})	2.228125	9.5492	1.4109	8.1383	2.0346
	4(D _{2h})	2.275000	10.3241	2.0488	8.2753	2.0688
	4(T _d)	2.337500	11.7482	3.1709	8.5773	2.1443
Fe	3(D _{∞h})	2.018750	1.8245	0.0165	1.8080	0.6027
	3(D _{3h})	2.053125	2.6859	0.3612	2.3247	0.7749
	4(D _{∞h})	2.018750	2.7492	0.0330	2.7163	0.6791
	4(D _{4h})	2.031250	4.1271	0.5165	3.6105	0.9026
	4(D _{2h})	2.065625	4.5215	0.7761	3.7455	0.9364
	4(T _d)	2.103125	5.2428	1.2736	3.9692	0.9923
Li	3(D _{∞h})	2.643750	2.2854	0.0690	2.2164	0.7388
	3(D _{3h})	2.956250	3.0540	0.4968	2.5571	0.8524
	4(D _{∞h})	2.637500	3.5083	0.1413	3.3670	0.8417
	4(D _{4h})	2.887500	5.1492	0.8323	4.3169	1.0792
	4(D _{2h})	3.018750	5.1384	0.9670	4.1713	1.0428
	4(T _d)	3.200000	5.5265	1.1803	4.3462	1.0866

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- [10] P.
- [11] G.
- [12] R.
- [13] T.
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- O
- [14] B.
- [15] S.
- [16] J.
- [17] M.
- [18] T.
- [19] C.

Table 3 (continue)

X	cluster	a	$-E_2$	E_3	$-E_T$	$-E_b$
C	3(D _{∞h})	1.3265625	12.2471	1.1786	11.0685	3.6895
	3(D _{3h})	1.753125	8.9623	2.8452	6.1171	2.0390
	4(D _{∞h})	1.343750	18.1992	2.0021	16.1971	4.0493
	4(D _{4h})	1.6421875	16.4515	4.2151	12.2364	3.0591
	4(D _{2h})	1.7953125	13.7052	4.3544	9.3507	2.3377
	4(T _d)	1.896875	13.0155	4.1762	8.8393	2.2098
Ge	3(D _{∞h})	2.468750	5.5276	0.2115	5.3161	1.7720
	3(D _{3h})	2.812500	7.0298	1.6851	5.3447	1.7816
	4(D _{∞h})	2.475000	8.3994	0.4120	7.9874	1.9969
	4(D _{4h})	2.759375	11.3753	2.3471	9.0282	2.2571
	4(D _{2h})	2.900000	11.2947	2.8929	8.4018	2.1004
	4(T _d)	3.087500	11.5891	3.2358	8.3533	2.0883
Si	3(D _{∞h})	2.275000	6.6103	0.2744	6.3359	2.1120
	3(D _{3h})	2.615625	8.0200	2.2932	5.7268	1.9089
	4(D _{∞h})	2.284375	9.9947	0.5249	9.4698	2.3675
	4(D _{4h})	2.559375	12.8155	3.0148	9.8008	2.4502
	4(D _{2h})	2.700000	12.5714	3.7774	8.7940	2.1985
	4(T _d)	2.881250	12.4131	3.9871	8.4260	2.1065

crystals is in progress in this laboratory. It is worth stressing that the present PEF is expected to be more suitable for bulk calculations, since it is calibrated with the bulk cohesive energy.

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