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Department of Physics, Middle East Technical University, Ankara[1])

A New Empirical Many-Body Potential Energy Function

Application to Microclusters: Elements in B.C.C., F.C.C., and H.C.P. Structures

By

Ş. ERKOÇ

A new empirical many-body potential energy function (PEF) has been proposed recently, and it has been successfully applied to microclusters of various elements. Using the new PEF the microcluster calculations are extended to several elements in b.c.c., f.c.c., and h.c.p. structures.

Kürzlich wurde eine neue empirische Vielkörper-Potentialenergiefunktion (PEF) vorgeschlagen und erfolgreich auf Mikrocluster verschiedener Elemente angewendet. Mit der neuen PEF werden die Mikroclusterberechnungen auf einige Elemente in k.r.z.-, k.f.z.- und h.d.p.-Strukturen ausgedehnt.

1. Introduction

Recently we have proposed a new empirical many-body potential energy function (PEF) [1] (hereafter we refer to it as I) and as an application we have investigated structural stability and energetics of three-atom and four-atom microclusters of various elements in different crystal structures.

The PEF comprises two- and three-body interactions. The two-body part has been expressed by a $(1/r^{2n} - 1/r^n)$-like pair potential in which each term is factorized by a Gaussian function, and the three-body part has been expressed in terms of the two-body functions. The explicit forms of the two-body function (U_{ij}) and the three-body function (W_{ijk}) are as follows:

$$U_{ij} = A\left[\left(\frac{r_0}{r_{ij}}\right)^{2n} \mathrm{e}^{-2\alpha(r_{ij}/r_0)^2} - \left(\frac{r_0}{r_{ij}}\right)^{n} \mathrm{e}^{-\alpha(r_{ij}/r_0)^2}\right] \tag{1}$$

and

$$W_{ijk} = B(U_{ij}f_{ijk} + U_{ik}f_{ikj} + U_{jk}f_{jki})\,, \tag{2}$$

where

$$f_{ijk} = \mathrm{e}^{-(r_{ik}^2 + r_{jk}^2)/r_0^2}\,, \tag{3}$$

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 equilibrium distance (r_0), equilibrium energy (ε_0), and force constant at equilibrium (k) of the dimer,

$$A = -4\varepsilon_0\,, \qquad \alpha = \ln(2)\,, \qquad n = \sqrt{\frac{r_0^2 k}{2|\varepsilon_0|}} - 2\alpha\,. \tag{4}$$

[1]) 06531 Ankara, Turkey.

The parameter (B) of the three-body functions is determined from the cohesive energy (Φ) of bulk material in a particular crystal structure,

$$\Phi = \sum_{i<j} U_{ij} + \sum_{i<j<k} W_{ijk} . \tag{5}$$

Details of the parametrization may be found in I.

In the present work we have parametrized the PEF for the following monatomic systems: Cs, K, and Na in b.c.c. crystal structure; Ca, Pb, Pd, and Pt in f.c.c. crystal structure, and Cd, Mg, Sc, Ti, and Zn in h.c.p. crystal structure. The necessary parameters used are given in Table 1 and the calculated parameters are given in Table 2. The three-body parameter B is positive for the h.c.p. elements Mg, Ti, and Zn, which means that the three-body potential has a negative contribution for these elements; B is negative for the rest of the elements considered in this work, that means the three-body potential has a positive contribution to the total energy for these elements.

Table 1
Parameters used in the calculations

element	r_0 (nm)	ε_0 (eV)	k (eV/nm^2)	Φ (eV) [8]	d_{nn} (nm) [8]	
Cs	0.447 [9]	−0.40 [9]	43 [9]	−0.80	0.524	
K	0.391 [9]	−0.52 [9]	61 [9]	−0.93	0.453	
Na	0.308 [9]	−0.73 [9]	107 [9]	−1.11	0.366	
Ca	0.428 [9]	−0.14 [9]	31 [9]	−1.84	0.395	
Pb	0.293 [9]	−0.85 [9]	458 [9]	−2.03	0.350	
Pd	0.257 [10]	−1.10 [10]	2315 [10]	−3.89	0.275	
Pt	0.234 [11]	−3.71 [11]	2437 [11]	−5.84	0.277	
					a (nm) [8]	c (nm) [8]
Cd	0.482 [11]	−0.04 [11]	10 [11]	−1.16	0.298	0.562
Mg	0.389 [9]	−0.05 [9]	12 [9]	−1.51	0.321	0.521
Sc	0.279 [11]	−1.65 [11]	472 [11]	−3.90	0.331	0.527
Ti	0.197 [11]	−1.23 [11]	1465 [11]	−4.85	0.295	0.468
Zn	0.235 [11]	−0.06 [11]	77 [11]	−1.35	0.266	0.495

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

element	A (eV)	n	B
Cs	1.60	1.890859	−2.023773
K	2.08	1.608210	−1.979834
Na	2.92	1.250439	−2.436817
Ca	0.56	3.117158	−0.145373
Pb	3.40	3.422940	−1.586818
Pd	4.40	6.950465	−0.681378
Pt	14.84	2.854446	−1.762003
Cd	0.16	4.002629	−0.097190
Mg	0.20	2.874987	1.112951
Sc	6.60	1.950414	−1.684201
Ti	4.92	3.421186	2.287793
Zn	0.24	4.566524	3.944883

2. Microcluster Calculations

We have considered three- and four-atom microclusters for the elements parametrized in Section 1. The geometry and the corresponding symmetry of the clusters considered in this work are given in Fig. 1, cluster energies and interatomic distances are given in Table 3.

a) b.c.c. elements: Cs, K, and Na are considered in this group. Triangular form of Cs_3 with D_{3h} symmetry and square planar form of Cs_4 with D_{4h} symmetry are found to be energetically more stable. There is no available data for these clusters in the literature. K_3 cluster with D_{3h} symmetry was experimentally found [2] as more stable; however, K_3 with C_{2v} symmetry was calculated [3] as more stable. The present calculation gives K_3 with D_{3h} symmetry as more stable, which is in agreement with experimental observation. K_4 cluster was not observed experimentally, however, the rhombic geometry with D_{2h} symmetry was calculated [3, 4] to be more stable. The present calculation gives the square geometry of K_4 with D_{4h} symmetry as more stable. Na_3 cluster with D_{3h} symmetry was experimentally found [2] as more stable; however, electronic calculations [3, 5, 6] give the C_{2v} symmetry as more stable. The present calculation gives Na_3 cluster with D_{3h} symmetry and Na_4 cluster with D_{4h} symmetry as more stable.

b) f.c.c. elements: Ca, Pb, Pd, and Pt are considered in this group. There is not any experimental observation for the microcluster of these elements. Pacchioni [7] calculated that the linear form of Ca_3 with $D_{\infty h}$ symmetry and triangular form with D_{3h} symmetry are almost energetically degenerate. The present calculation shows that the triangular form of Ca_3 with D_{3h} symmetry is energetically more stable. For Ca_4 cluster the tetragonal form with T_d symmetry was calculated [4, 5, 7] to be more stable. The present calculation is in agreement with literature values for Ca clusters. For Pb no cluster data is available in the literature. The present calculation gives triangular form of Pb_3 with D_{3h} symmetry and tetragonal form of Pb_4 with T_d symmetry as energetically more stable. The rhombic and tetragonal forms of Pb_4 are energetically very close to each other, but the tetragonal form is favorable. There is no information about the Pd_3 cluster in the literature and the tetragonal form of Pd_4 with T_d symmetry was calculated [5] as more stable. The present calculation gives the triangular form of Pd_3 with D_{3h} symmetry and the tetragonal form of Pd_4 with T_d symmetry as more stable, which is in agreement with the literature value. No information is available for Pt_3 cluster, but the tetragonal form of Pt_4 with T_d symmetry was calculated [5] as more stable. The present calculation gives the triangular form of Pt_3 with D_{3h} symmetry and the tetragonal form of Pt_4 with T_d symmetry as energetically more stable. The agreement with the literature value and the present result for Pt_4 is also good.

c) h.c.p. elements: Cd, Mg, Sc, Ti, and Zn are considered in this group. No information is available in the literature for Cd and Zn microclusters. Pacchioni [7] calculated

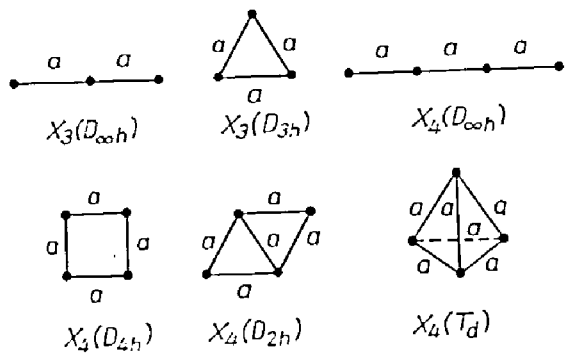

Fig. 1. The geometry and the corresponding symmetry of three-atom and four-atom microclusters

Table 3

Calculated interatomic distances (in nm) and cluster energies (in eV). 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	$-E_T$	$-E_b$
Cs	$3(D_{\infty h})$	0.4468750	0.8266	0.0182	0.8083	0.2694
	$3(D_{3h})$	0.4781250	1.1504	0.2362	0.9143	0.3048
	$4(D_{\infty h})$	0.4468750	1.2535	0.0365	1.2171	0.3043
	$4(D_{4h})$	0.4718750	1.8438	0.3479	1.4959	0.3740
	$4(D_{2h})$	0.4893750	1.8972	0.4497	1.4475	0.3619
	$4(T_d)$	0.5156250	2.0293	0.5738	1.4555	0.3639
K	$3(D_{\infty h})$	0.3906250	1.0820	0.0253	1.0567	0.3522
	$3(D_{3h})$	0.4218750	1.4911	0.2877	1.2034	0.4011
	$4(D_{\infty h})$	0.3900000	1.6457	0.0515	1.5942	0.3985
	$4(D_{4h})$	0.4150000	2.4261	0.4410	1.9851	0.4963
	$4(D_{2h})$	0.4312500	2.4746	0.5535	1.9211	0.4803
	$4(T_d)$	0.4550000	2.6525	0.7001	1.9528	0.4882
Na	$3(D_{\infty h})$	0.3081250	1.5345	0.0484	1.4861	0.4954
	$3(D_{3h})$	0.3437500	2.0365	0.4109	1.6255	0.5418
	$4(D_{\infty h})$	0.3081250	2.3404	0.0969	2.2435	0.5609
	$4(D_{4h})$	0.3375000	3.3428	0.6198	2.7230	0.6807
	$4(D_{2h})$	0.3531250	3.3493	0.7509	2.5984	0.6496
	$4(T_d)$	0.3743750	3.5425	0.8992	2.6433	0.6608
Ca	$3(D_{\infty h})$	0.4268750	0.2841	0.0004	0.2837	0.0946
	$3(D_{3h})$	0.4287500	0.4200	0.0082	0.4118	0.1373
	$4(D_{\infty h})$	0.4262500	0.4282	0.0007	0.4275	0.1069
	$4(D_{4h})$	0.4212500	0.6515	0.0128	0.6387	0.1597
	$4(D_{2h})$	0.4281250	0.7123	0.0185	0.6938	0.1735
	$4(T_d)$	0.4300000	0.8396	0.0324	0.8072	0.2018
Pb	$3(D_{\infty h})$	0.2931250	1.7196	0.0223	1.6973	0.5658
	$3(D_{3h})$	0.3006250	2.5151	0.4861	2.0290	0.6763
	$4(D_{\infty h})$	0.2934375	2.5889	0.0441	2.5448	0.6362
	$4(D_{4h})$	0.2984375	3.8067	0.6485	3.1582	0.7895
	$4(D_{2h})$	0.3040625	4.1824	1.0018	3.1806	0.7951
	$4(T_d)$	0.3131250	4.7056	1.5211	3.1844	0.7961
Pd	$3(D_{\infty h})$	0.25703125	2.2022	0.0103	2.1919	0.7306
	$3(D_{3h})$	0.2578125	3.2978	0.3003	2.9975	0.9992
	$4(D_{\infty h})$	0.25703125	3.3044	0.0206	3.2839	0.8210
	$4(D_{4h})$	0.2571875	4.5919	0.3325	4.2593	1.0648
	$4(D_{2h})$	0.2581250	5.5044	0.6523	4.8521	1.2130
	$4(T_d)$	0.2587500	6.5800	1.1808	5.3992	1.3498
Pt	$3(D_{\infty h})$	0.2340625	7.5468	0.1181	7.4288	2.4762
	$3(D_{3h})$	0.2428125	10.8903	2.2274	8.6629	2.8876
	$4(D_{\infty h})$	0.2343750	11.3816	0.2329	11.1487	2.7872
	$4(D_{4h})$	0.2406250	16.8180	3.0849	13.7331	3.4333
	$4(D_{2h})$	0.2465625	18.0529	4.4790	13.5739	3.3935
	$4(T_d)$	0.2565625	19.8123	6.3068	13.5056	3.3764
Cd	$3(D_{\infty h})$	0.4812500	0.0806	0.0001	0.0806	0.0269
	$3(D_{3h})$	0.4825000	0.1200	0.0016	0.1184	0.0395
	$4(D_{\infty h})$	0.4812500	0.1213	0.0001	0.1211	0.0303
	$4(D_{4h})$	0.4768750	0.1795	0.0022	0.1773	0.0443
	$4(D_{2h})$	0.4818750	0.2022	0.0035	0.1987	0.0497
	$4(T_d)$	0.4831250	0.2400	0.0063	0.2337	0.0584

Table 3 (continued)

	cluster	a	$-E_2$	E_3	$-E_T$	$-E_b$
Mg	$3(D_{\infty h})$	0.3862500	0.1017	−0.0011	0.1028	0.0343
	$3(D_{3h})$	0.3837500	0.1495	−0.0238	0.1732	0.0577
	$4(D_{\infty h})$	0.3856250	0.1534	−0.0022	0.1556	0.0389
	$4(D_{4h})$	0.3718750	0.2331	−0.0424	0.2755	0.0689
	$4(D_{2h})$	0.3803125	0.2533	−0.0556	0.3089	0.0772
	$4(T_d)$	0.3803125	0.2970	−0.0977	0.3947	0.0987
Sc	$3(D_{\infty h})$	0.2787500	3.4057	0.0620	3.3437	1.1146
	$3(D_{3h})$	0.2943750	4.8114	0.8744	3.9370	1.3123
	$4(D_{\infty h})$	0.2781250	5.1660	0.1269	5.0390	1.2598
	$4(D_{4h})$	0.2900000	7.7459	1.3399	6.4059	1.6015
	$4(D_{2h})$	0.2993750	8.0426	1.7546	6.2879	1.5720
	$4(T_d)$	0.3137500	8.7695	2.3549	6.4147	1.6037
Ti	$3(D_{\infty h})$	0.1956250	2.4875	−0.0503	2.5378	0.8459
	$3(D_{3h})$	0.1934375	3.6593	−1.2172	4.8765	1.6255
	$4(D_{\infty h})$	0.1953125	3.7453	−0.1022	3.8475	0.9619
	$4(D_{4h})$	0.1881250	5.5196	−2.0326	7.5522	1.8880
	$4(D_{2h})$	0.1918750	6.1512	−2.8119	8.9632	2.2408
	$4(T_d)$	0.19171875	7.2386	−4.9826	12.2213	3.0553
Zn	$3(D_{\infty h})$	0.23390625	0.1206	−0.0037	0.1243	0.0414
	$3(D_{3h})$	0.23109375	0.1780	−0.1015	0.2796	0.0932
	$4(D_{\infty h})$	0.2334375	0.1811	−0.0075	0.1886	0.0472
	$4(D_{4h})$	0.2268750	0.2569	−0.1458	0.4027	0.1007
	$4(D_{2h})$	0.22984375	0.2970	−0.2291	0.5261	0.1315
	$4(T_d)$	0.22953125	0.3519	−0.4120	0.7640	0.1910

that Mg_3 cluster with D_{3h} symmetry and $D_{\infty h}$ symmetry are energetically almost degenerate. Mg_4 cluster with T_d symmetry was calculated [4, 5, 7] as more stable. Triangular form of Sc_3 with D_{3h} symmetry was experimentally found [2, 5, 8] more stable. No information is available in the literature about Sc_4. Ti_3 with D_{3h} symmetry and Ti_4 with T_d symmetry were calculated [5] as more stable. The present calculation gives the three- and four-atom microclusters with D_{3h} and T_d symmetry, respectively, more stable for all the elements considered in this group. The present results are in good agreement with the literature values.

As a conclusion, the present PEF gives qualitatively reasonable results for the stability of microclusters of various elements in different crystal structures.

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Note added in proof:

There is an error in the A values of Table 2 in [1], they should be calculated as $A = -4\varepsilon_0$.