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Energetics of Spherical Clusters

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Abstract

The energetics of spherical clusters of elements Fe in bcc, Ca and Pb in fcc, and C in diamond structure have been investigated by using emprical many-body potential energy function which contains two- and three-body inteactions. In the variation of average interaction energy per atom (E_b) versus cluster size (N_{sh}; number of shells) only carbon clusters have magic numbers at 5, 8, 11 and 14 shells. E_b versus N_{sh} becomes smooth after 15 shells for carbon, however this variation becomes smooth for the other elements after 10 shells. The variation of two-body to three-body interaction energy versus cluster size becomes almost constant after 10 shells for all elements considered. Energetic cluster size effect has been also investigated for the elements considered.

In recent years there has been increasing interest in structural properties and energetics of various clusters [1-4]. To investigate different properties of elements such as bulk, surface, and clusters at atomistic level, computer simulations using empirical potential energy function have been extensively used [5-6].

In this work we have studied the energetics of spherical ideal clusters of several elements in fcc, bcc, and diamond structures. We used an empirical many-body potential energy function (PEF) previously [7,8] and succesfully applied to the microclusters of several elements in various crystal structure. The PEF includes two-and three-body interactions

$$\Phi = \Phi_2 + \Phi_3 = \sum_{i<j} U_{ij}(r_{ij}) + \sum_{i<j<k} W_{ijk}(r_{ij}, r_{ik}, r_{jk}), \tag{1}$$

where two-body (U_{ij}) and three-body(W_{ijk}) interactions are defined respectively, as

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

$$W_{ijk} = B[U_{ij}f_{ijk} + U_{ik}f_{ikj} + U_{jk}f_{jki}], \tag{3}$$

where

$$f_{ijk} = e^{-(r_{ik}^2 + r_{jk}^2)/r_0^2}; \tag{4}$$

similarly, f_{ikj} and f_{jki} have the same form as f_{ijk} with suitable indices, and r_{ij} is the interatomic distance between atoms i and j.

The present PEF satisfies the bulk cohesive energy per atom Φ and crystal stability condition (Φ vs atomic value). It also gives reasonable results for structural stability and energetics of microclusters (3-4 atoms) for the elements parameterized [7-8].

We extended the calculations for large clusters in spherical form with crystalline structure. The size of the clusters extended from first neighbour shell up to 25 shells for the elements in fcc, bcc and diamond structure parameterized for this PEF. We performed the calculations keeping the clusters in ideal structures: we did not optimize the geometry of the clusters. In other words, we performed a static calculation.

In the present work, the PEF has been applied to investigate energetics of spherical clusters including up to 25 shells of atoms. The present PEF was parameterized for the following monatomic systems: Cs, K, Na, Fe, Li in bcc crystal structure; Ca, Pb, Pd, Ag, Al, Au, Cu, and Ni in fcc structure, and C, Ge, and Si in diamond structure. The calculated average interaction energy per atom versus cluster size for the unrelaxed (ideal) spherical clusters looks reasonable for all lthe elements parameterized for the first few shells. However, as the number of shells increases average interaction energy per atom remains above the bulk cohesive energy of the corresponding element only for Fe, Ca, Pb, and C. The parameters used in calculations are given in Table 1. This trend might change if the calculations were performed by relaxation via molecular dynamics.

Table 1. Parameters used in the calculations. α=ln(2)[7,8].

Element	A(eV)	n	$r_0(A^0)$	B
Ca	0.56	3.117158	4.28	-0.145373
Pb	3.40	3.422940	2.93	-1.586818
Fe	3.60	3.195342	2.02	-1.061661
C	24.84	1.680481	1.24	–17.293200

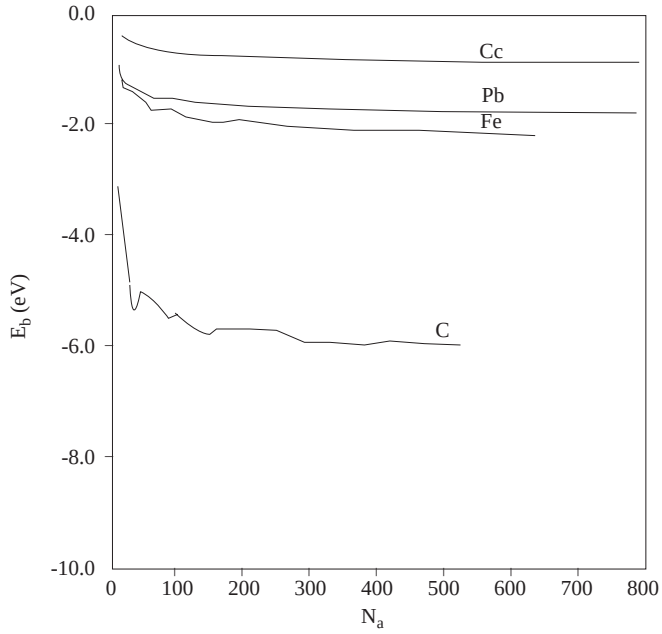


Figure 1. Variation of average interaction energy per atom versus the number of atoms.

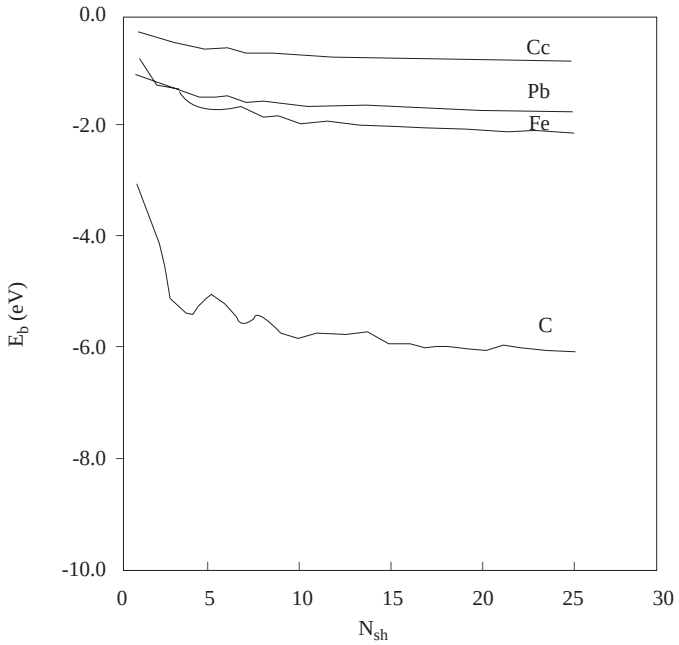
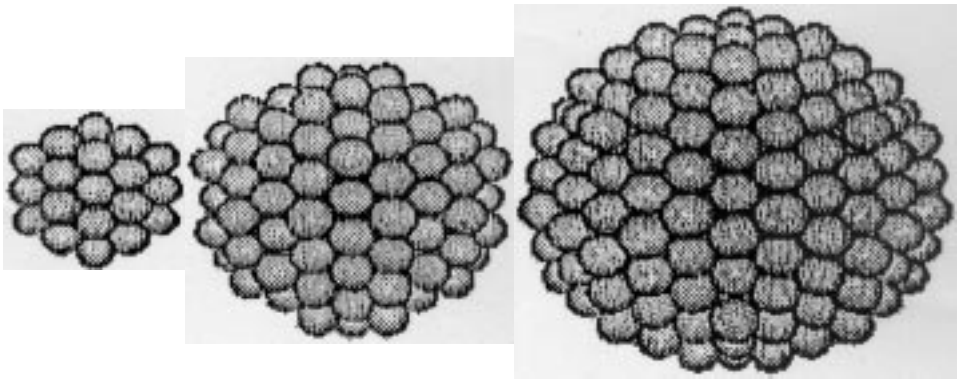


Figure 2. Variation of average interaction energy per atom versus the number of shells.



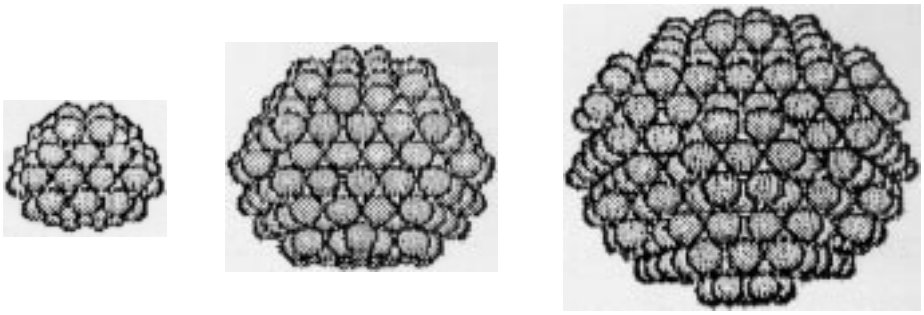
N_{sh} =5
N_a =59

N_{sh} =15
N_a =285

N_{sh} =25
N_a =623

Spherical clusters in bcc structure

Figure 3a.



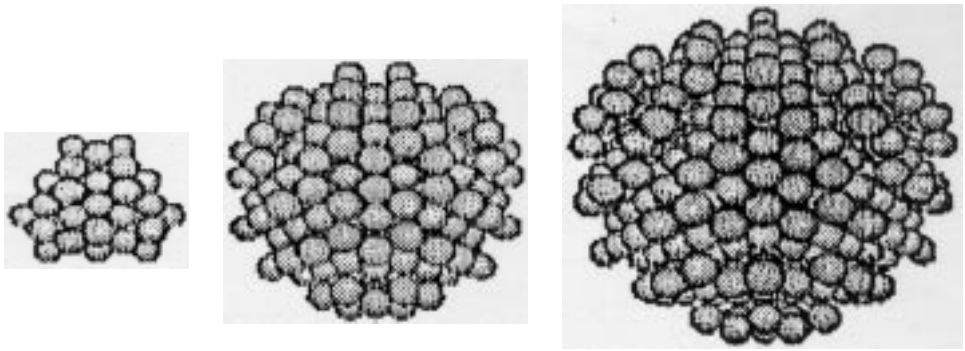
N_{sh} =5
N_a =79

N_{sh} =15
N_a =381

N_{sh} =25
N_a =791

Spherical clusters in fcc structure

Figure 3b.



N_{sh} =5 N_a =47 N_{sh} =15 N_a =275 N_{sh} =25 N_a =525

Spherical clusters in diamond structure

Figure 3c.

For the elements Fe, C, Ca, and Pb the variation of E_b versus the cluster size, namely as the number of atoms (N_a) and the number of shells (N_{sh}), is shown in Figs. 1 and 2, respectively. The view of the spherical clusters for the shells 5, 15, and 25 for the structures fcc, bcc, and diamond are shown in Fig. 3. There are certain cluster shell sizes that are prominent: the magic numbers. The relative abundance maxima reflect especially stable or in same sense closed shells structure [3]. This property appears particularly for carbon spherical clusters. For the other elements (Fe, Ca, Pb) the energy versus cluster size curves are almost smooth. Magic numbers for C are 5, 8, 11, and 14. They satisfies the relationship N_{sh}=3m-1; m=2,3. . ., with groupings of four.

The behavior of two-body interaction energy per atom as a function of cluster size as illustrated in Fig. 4 represents a smooth decreasing for Ca, Fe, and Pb as cluster size increases. For C, there is a sharp decrease up to fourth shell. The three-body interaction energy per atom as a function of the number of shells are illustrated in Fig. 5 We observe that as N_{sh} increases the contribution of the average three-body interaction energy per atom increases rapidly for C element. However for the other elements the increase is much more gradual and it is constant after 10 shells. In Fig. 6, the behavior of the ratio of total two-to three-body interaction energy versus cluster size becomes almost constant after 10 shells for all elements considered. However, for small structures (N_{sh} <5) this ratio decreases very sharply for Fe, meaning that the contribution of three-body interaction on Fe microclusters is relatively very small but its contribution increases and for a certain cluster size the ratio ($|E_2/E_3|$) becomes constant. This rapid change in $|E_2/E_3|$ also appears in Ca microclusters. From this diagram (Fig. 6) one can conclude that the contribution of three-body interaction is considerably large for C and Pb. Although the crystal structure of C and Pb are different, the variation of $|E_2/E_3|$ versus cluster size

for these elements are close to each other.

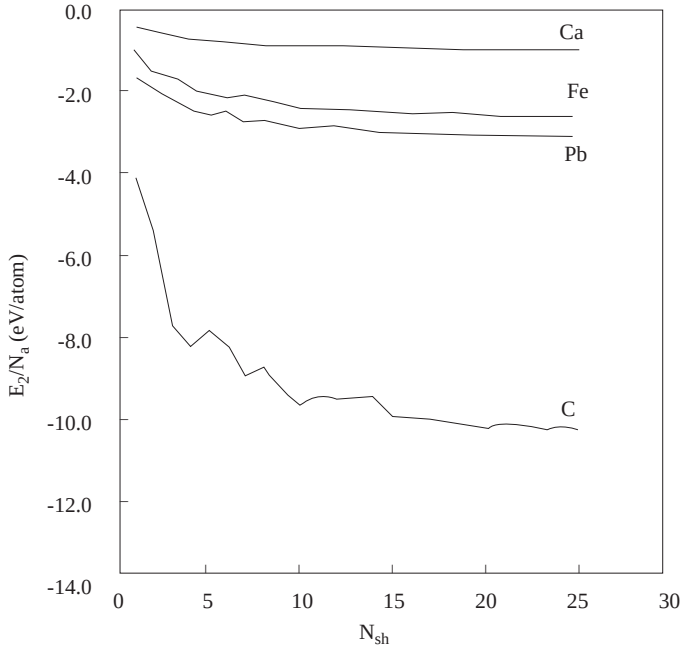


Figure 4. Variation of two-body interaction energy per atom versus cluster size (N_{sh}).

The size effect is one of the important properties in clusters. Energetic cluster size effect shows the convergency of energy of cluster with respect to the cluster size. The energy expression, namely average interaction energy per atom in the cluster (E_b) with respect to size is given by [9]

$$E_b = E_v + E_s N_a^{-1/3} + E_c N_a^{-2/3}, \tag{5}$$

where E_v, E_s, and E_c represent the volume energy, the surface energy, and the curvature energy of the cluster, respectively. N_a is the number of atoms in the cluster, which is the size parameter in Eq. 5. The convergency of energy in Eq. 5 could be a measure of the interaction range of the PEF used. In Eq. 5 the energy parameters E_v, E_s, E_c are determined by fitting the data to the function. In some cases the first two terms in Eq. 5 are considered and the parameters E_v and E_s are determined by a linear fit. One can determine the set of size parameters E_v, E_s, E_c by a quadratic fit procedure.

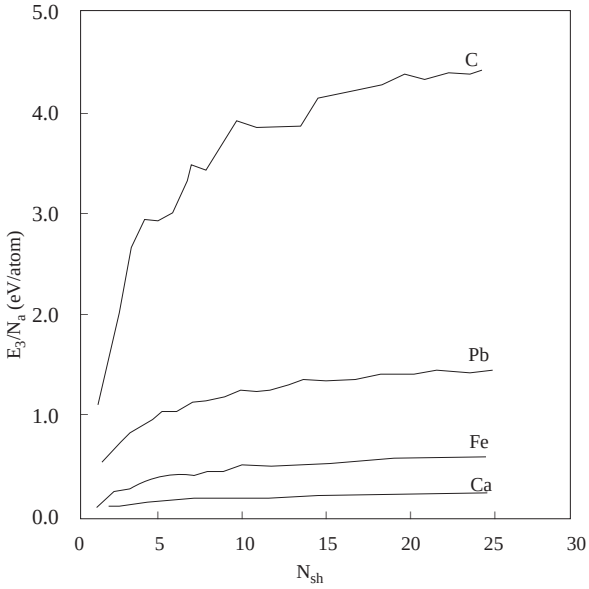


Figure 5. Variation of three-body interaction energy per atom versus cluster size (N_{sh}).

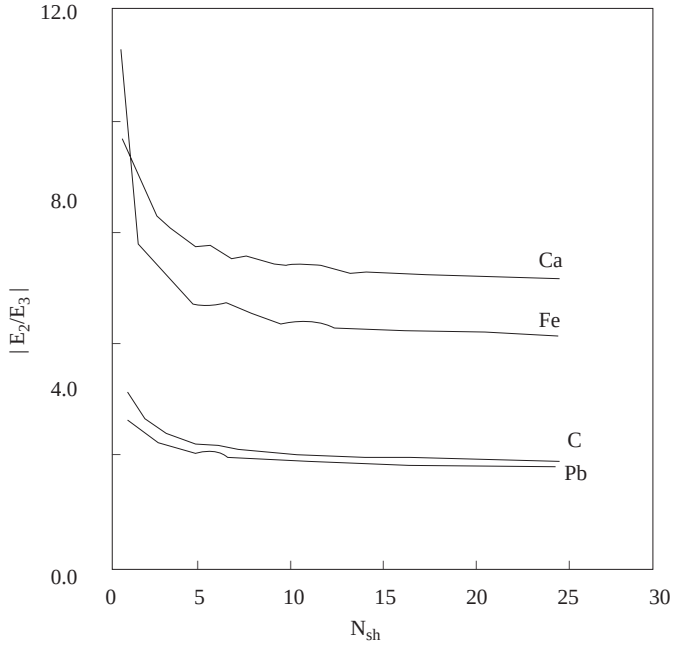


Figure 6. The ratio of two- to three-body interaction energy versus cluster size (N_{sh}).

The energy size parameters of the clusters considered in this work are determined by applying linear and quadratic fit of the data. The calculated values are given in Table 2. From the calculated values one can see that the present PEF for carbon is better in energy convergency with respect to the cluster size.

Table 2. Energetic size parameters of spherical clusters.

Element	Linear fit		Quadratic fit		
	E_v	E_s	E_v	E_s	E_c
Ca	-1.0036	1.5282	-1.0448	1.9832	-0.8341
Pb	-1.9578	1.9293	-1.9393	1.7456	0.3736
Fe	-2.5187	3.3606	-2.3872	2.2097	1.1082
C	-6.8704	6.4097	-6.6205	4.3853	3.1728

As a conclusion the present PEF describes well the energetics of spherical clusters of C, Fe, Ca, and Pb. From the results of calculations it is seen that the contribution of many-body effect is considerable and it must be taken into account for realistic simulations. On the other hand, the present PEF also describes the convergency in energy as cluster size increases.

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