



Many-Body Interaction and Computer Simulations for the Cohesive Energy of Spherical Metallic Nanocrystals

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Many-body interaction potential energy function is used to predict the structural stability and cohesive energy of Molybdenum (Mo) and Tungsten (W) spherical metallic nanocrystals by computer simulations. The model proposed is Ercok's potential energy function comprising two- and three-body terms. The model applies successfully to BCC elements and predicts the size dependence of the cohesive energy of nanocrystals. This prediction agrees with experimental measurements on Mo and W.

Keywords: Many-Body Interaction Potential, Molecular Dynamics at 0 K Method, Cohesive Energy, Structural Stability.

RESEARCH ARTICLE

1. INTRODUCTION

After the invention of the tunneling microscope in 1985, it became possible to construct a crystal atom-by-atom, leading to a new field of science called "nanoscience."¹ It is observed that the properties of materials at the nano-scale level can be substantially different from macro-scale levels. This is very apparent with nanocrystals, where researchers verified experimentally and theoretically that some intriguing magnetic, electric, optical, mechanical and thermo-dynamical properties were not realized before with large crystals, and this brought up a new range of promising applications. It is believed that these drastic changes in the properties are due to the large ratio of the number of surface atoms to their volume in nanocrystals. On this scale, it is also evident that structure transitions which may occur under certain conditions lead to changes in the physical and chemical properties of nanocrystals.

Up-to-date, most of the experimental work in nanoscience falls into two broad categories: preparation of nanocrystals,²⁻⁷ and measuring their magnetic, electrical, etc., properties.⁸⁻¹⁴ On the theoretical side,¹⁵⁻²⁷ there has been much effort expended towards modeling the interatomic potential energy, which controls the internal interactions within nanocrystals, using many approaches like computer simulation, *ab initio* calculations and other techniques to predict structure transition and super characteristics.

Among many physical quantities, the cohesive energy is of special interest since all the thermodynamical quantities like heat capacity, surface tension, etc., may be derived from it. The cohesive energy of a crystal is defined as the energy that must be added to the crystal to separate its components into neutral free atoms at rest, at infinite separation.²⁸ Cohesive energy depends on the size of nanocrystals, type of atoms involved, the shape and structure.

For nanocrystals, a careful measurement of the cohesive energy proved its size dependence,²⁹ while it is constant for bulk crystals. Many theoretical models and techniques were developed to predict the size dependence of the cohesive energy.¹⁵⁻²⁶ Although all of these models successfully predict the size dependence of the cohesive energy, some of them were phenomenological^{16,23} and not computational in a sense they cannot justify some of the criteria related to the crystals such as structure transition. Among them, Qi et al.¹⁶ modified a model upon calculating the surface energy of a solid at 0 K. They did not pay any attention to the structure or shape of the crystals. A different approach was used by Sun et al.¹⁷ in the Bond-Length-Strength (BLOS) model. The model indirectly accounts for shape and size to calculate the melting temperature which is related to the cohesive energy and predicts its behavior well.^{15,30-31} Nevertheless, the model ignored structure and does not give any idea about structure transition. Both Jiang et al.¹⁸ and Chun Cheng et al.²¹ groups used the same model to predict the cohesive energy and fit that to experimental data for Molybdenum (Mo), Tungsten (W),¹⁸ and to Iron (Fe), Copper (Cu), Gold (Au)²¹ respectively. The two groups had good fit and showed the size dependence

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of the cohesive energy but the model's deficiency was not considering both the shape and structure of the crystal. The liquid drop model applied successfully to explain the mass of the atomic nuclei is used here by Nanda et al.¹⁵ to justify the size dependence of the cohesive energy of low dimensional systems. The expression for cohesive energy given is exactly the same as that of Qi et al.,¹⁶ so it takes care of size but neither of shape nor structure. A simple model suggested by Qi et al.²⁵ to fit the experimental data for Mo and W works well for that purpose, but the authors made too many assumptions that left the model applicable only under certain assumptions.

There are many research groups that used the semi-empirical potential energy functions and computer simulations to study the behavior of the cohesive energy of nanocrystals. Qi et al.¹⁹ tried to fit the experimental data of Mo and W by using the well known two-body Lennard-Jones potential energy function (PEF). The size dependence is again there but the ratio of the cohesive energy of the nanocrystal to that of the bulk for the above mentioned elements did not match the data. Another problem with this model is that it included only a two-body term which is not enough for elements other than the rare gases to give absolute stability of the system. Another group, Barakat et al.²² used two-body PEF and achieved excellent fit for Mo and W using Mie-Type potential function with (m, k) as $(6, 5)$. The use of this model had two main problems. First, as the previous model, it includes only two-body part and the second is that it contains two power terms of the same order so that both of them are considered to be short range terms. It was implicitly assumed in the model that long range interaction is ignored which is physically unacceptable. Another good model that accommodates size, shape, and structure to calculate the cohesive energy of a nanocrystal was presented by Qi.²⁰ But his work is limited since it only applies to Chromium (Cr) and was not generalized to other elements. The last model to be discussed here is a phenomenological model by Aslam et al.²³ which uses empirical PEF that comprises two body terms of long range as coulomb and Van Der Waals as Lennard-Jones terms.

Recently our group²⁴ designed a model which includes both two and three body terms in the PEF. The two body term was a Mie-Type with (m, k) as $(8, 4)$. So one of them is for short range and the other is for long range terms. The three bodies were Teller-Axilord triple-dipole term. The only assumption made for this model was to consider the crystal as spherical, so shape factor was ignored. The model applies to all elements in the periodic table exceptionally and shows stability. The size dependant potential parameter (SDPP) method was used in that project.

In this paper the energy minimization (EM) method has been proposed to perform the cohesive energy and structural stability calculations. This method is a subcategory

of molecular dynamics where the temperature is considered to be 0 K. The method although simple in principle, proves to be powerful in the results it predicts.

2. MODEL AND POTENTIAL ENERGY FUNCTION

To construct the model, we assume that a spherical metallic nanocrystal in the nanometer size is generated from ideal BCC crystalline structures, and its internal structure is the same as the bulk crystal. An atom is taken as a central one and the first nearest-neighbor distance is considered as the radius of the first shell and second nearest-neighbor distance as the radius of the second shell, and so on. The number of shells in the nanocrystal, the radius of the nanocrystal R_{cut} , the number of atoms in each shell and the total number of atoms (N) in the nanocrystal can all be easily obtained.

The potential energy of N interacting atoms can be expressed as a many-body expansion:

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

Where ϕ_2, ϕ_3, \dots are the two, three-body... interaction energies respectively. In the present work, two and three body atomic interactions are adopted to simulate and reproduce the cohesive energy and structure-related properties. The two body PEF, uses simplified statistical mechanical formalism for calculating various thermodynamical properties and enabled many early researchers to run simulation calculations with relatively less powerful computers. However, it produces results inconsistent with many experiments.³⁰ In addition, the first order approximation (two-body PEF) is particularly inappropriate for atoms other than those with a closed-shell structure.³¹

An empirical potential energy function PEF to describe the three-to-thirteen-atom microclusters was suggested in 1989 Refs. [32, 33] and modified in 1990³⁴ by Erkoc. This PEF works well for the microclusters of elements at different structures.^{32, 33} There are different empirical PEF's to describe the interatomic interaction of bulk and small clusters, like those suggested by Person et al., Stillinger and Weber, and Tersoff. Although their predictions of the structural stability and energy are fairly good, they require an evaluation of three, nine, and eleven parameters respectively. However, the PEF proposed by Erkoc (EPEF) needs the evaluation of only two parameters. The explicit form of EPEF for N interacting atoms is:

$$\Phi = c_2\phi_2 + c_3\phi_3 \quad (2)$$

Where

$$\phi_2 = \sum_{\substack{i,j=1 \\ i \neq j}}^N U(r_i, r_j) \quad (3)$$

And

$$\phi_3 = \sum_{\substack{i,j,k=1 \\ i \neq j \neq k}} W[r_i, r_j, r_k] \quad (4)$$

ϕ_2 and ϕ_3 are the two-body and three-body interaction energies respectively. The two-body PEF is a combination of a repulsive and an attractive parts factorized by Gaussian terms. The three-body PEF is expressed in terms of the two-body part. More explicitly $U(r_i, r_j)$ and $W[r_i, r_j, r_k]$ are expressed as:

$$U(r_i, r_j) = A \left[\left(\frac{r_0}{r_{ij}} \right)^{2n} e^{-2\alpha[r_{ij}/r_0]^2} - \left(\frac{r_0}{r_{ij}} \right)^n e^{-\alpha[r_{ij}/r_0]^2} \right] \quad (5)$$

And

$$W[r_i, r_j, r_k] = U_{ij}f_{ijk} + U_{ik}f_{ikj} + U_{jk}f_{jki} \quad (6)$$

With

$$f_{ijk} = e^{-(r_{ik}^2 + r_{jk}^2)/r_0^2} \quad (7)$$

Similarly, f_{ikj} and f_{jki} have the same form as f_{ijk} with suitable indices, r_{ij} is the interaction distance between atom i and atom j . The parameters A , α and n are found in terms of the force constant k , equilibrium distance r_0 and equilibrium energy ε_0 through the three stability conditions:

$$U_{ij}|_{r_{ij}=r_0} = \varepsilon_0 \quad (8)$$

$$\left. \frac{\partial U_{ij}}{\partial r_{ij}} \right|_{r_{ij}=r_0} = 0 \quad (9)$$

$$\left. \frac{\partial^2 U_{ij}}{\partial r_{ij}^2} \right|_{r_{ij}=r_0} = k \quad (10)$$

Simple calculations give the values of the three parameters as:

$$A = -4\varepsilon_0 \quad (11)$$

$$\alpha = \ln(2) \quad (12)$$

and

$$n = \sqrt{\frac{r_0^2 k}{2|\varepsilon_0|}} - 2\alpha \quad (13)$$

The total interaction energy is expressed as:

$$\Phi = c_2\phi_2 + c_3\phi_3 \quad (14)$$

where c_2 and c_3 are free parameters to be determined through the stability condition $\partial\Phi/\partial V = 0$, which leads to the relation:

$$c_2\phi'_2 + c_3\phi'_3 = 0 \quad (15)$$

where

$$\phi'_2 = \partial\phi_2/\partial V \quad (16)$$

and

$$\phi'_3 = \partial\phi_3/\partial V \quad (17)$$

The parameters c_2 and c_3 can be found by solving Eqs. (14) and (15) simultaneously by calculating ϕ_2, ϕ_3, ϕ'_2 and ϕ'_3 , the values of c_2 and c_3 are determined as:

$$c_3 = \Phi/[\phi_3 - \phi'_3\phi_2/\phi'_2] \quad (18)$$

and

$$c_2 = -c_3\phi'_3/\phi'_2 \quad (19)$$

Table I. Spectroscopic properties of Mo and W.

Element	r_0 [Å]	$-\varepsilon_0$ [eV]	k [eV/Å ²]	d_{nn} [Å]	ϕ [Å]
Mo	1.938	4.38	40.61	2.72	-6.20
W	2.425	5.00	20.00	2.74	-8.55

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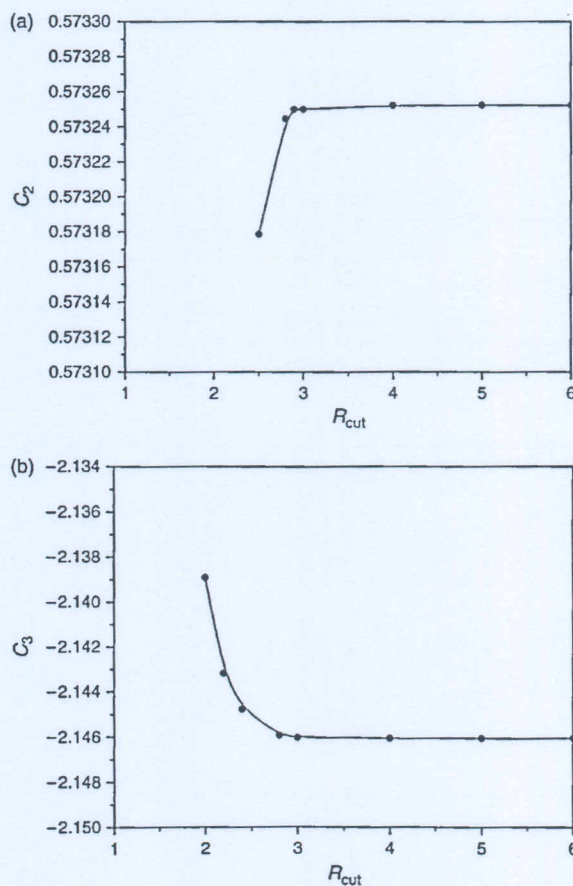


Fig. 1. (a) Size dependence of the two-body part of EPEF (c_2) of body-centered cubic structure of Molybdenum as a function of nanocrystal size R_{cut} . (b) Size dependence of the three-body part of EPEF (c_3) of body-centered cubic structure of Molybdenum as a function of nanocrystal size R_{cut} .

3. NUMERICAL RESULTS AND DISCUSSION

The above described model and PEF have been investigated for both Molybdenum and Tungsten metallic nanocrystals. The parameters used in the calculation of the cohesive energy of Mo and W are given in Table I.

The parameters A and n are calculated directly from Eqs. (11)–(13), while the parameters c_2 and c_3 are functions of the number of atoms in the nanocrystal N as shown in Figures 1(a, b) for Mo and Figures 2(a, b) for W. So ultimately c_2 and c_3 with A and n are given in Table II.

The parameters c_2 and c_3 decide the contribution of the two and three-body parts of the cohesive energy. The three-body part of EPEF is positively contributing to the total energy of the crystal and works as a fine tuning adjustment to the cohesive energy. As can be seen from the Figures 1 and 2, c_2 and c_3 are size dependant that reach- to seven

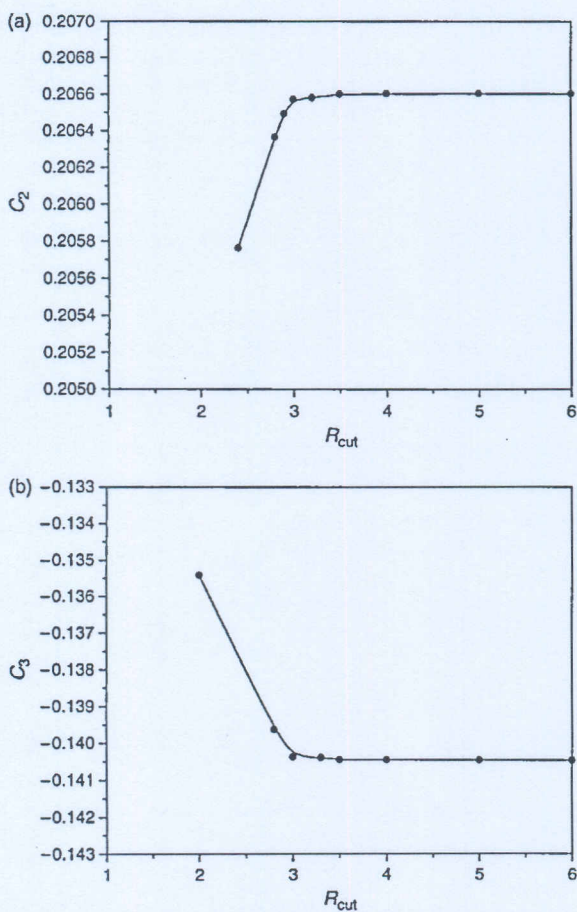


Fig. 2. (a) Size dependence of the two-body part of EPEF (c_2) of body-centered cubic structure of Tungsten as a function of nanocrystal size R_{cut} . (b) Size dependence of the three-body part of EPEF (c_3) of body-centered cubic structure of Tungsten as a function of nanocrystal size R_{cut} .

Table II. The two and three-body parts of EPEF (c_2 and c_3) for BCC structure of Molybdenum and Tungsten and the calculated values of A and n .

Element	Structure	c_2	c_3	$-A$ [eV]	n
Mo	BCC	0.573252	-2.146064	17.52	2.786416
W	BCC	0.206602	-0.140455	20.00	2.043174

digit accuracy-their saturation values at a cut-off radius of the nanocrystal of $4d_{nn}$ for the two elements considered in this work. This conclusion was verified previously for many other elements.³²

The energy minimization (EM) method has been implemented by employing the PEF and search over configuration space until the minimum is located. According to EPEF the minimum cohesive energies for both Mo and W have been calculated as a function of N , and the relative minimum energy ϕ_a/ϕ_0 has been plotted for BCC structure as shown in Figure 3, where ϕ_0 is the bulk cohesive energy listed in Table I. The normalized experimental data reported by Kim et al. in 2002 Ref. [29] are denoted by arrows for Mo at $N = 2000$ and for W at $N = 7000$ atoms. It is clear from the figures that the cohesive energy is size dependant and converges to 63.3% of the bulk at $N = 6183$ (BCC-Mo) and to 58.2% of it at $N = 6183$ (BCC-W). The predicted calculation of the cohesive energy using EPEF model is lower than the reported experimental results of Mo and W. A quantitative comparison between the experimental and theoretical results for the relative cohesive energies for BCC is presented in Table III at $N = 2000$ and 7000 atoms.

However, under the assumptions made where the interatomic distances at equilibrium were equal and the nanocrystal is spherical, the present results are acceptable.

As was mentioned before, the only available experimental values of the cohesive energies are those of Mo and W nanocrystals.^{29,36} It is reported that the cohesive

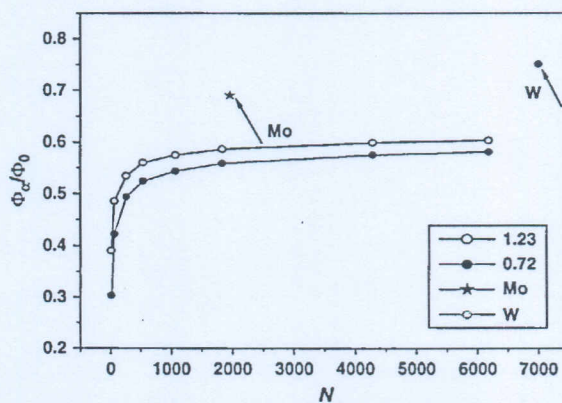


Fig. 3. Crystal size dependence of the relative cohesive energy of body-centered cubic spherical Molybdenum and Tungsten nanocrystals according to EPEF.

Table III. comparison between the experimental and theoretical results for the relative cohesive energies for both BCC and FCC according to EPEF model.

Element	Number of atoms N	Theoretical EPEF	Theoretical Mie-type (m, k) is (12, 6) ¹⁹	Experimental ratio
Mo	2000	0.58	0.84	0.68562
	7000	0.633	0.87	—
W	2000	0.56	0.84	0.75121
	7000	0.582	0.87	—

energy of Mo nanocrystal of the size $N = 2000$ is -4.25 eV/atom, whereas the cohesive energy of the bulk Mo is -6.2 eV/atom. On the other hand, for the W nanocrystal of size $N = 7000$, its cohesive energy is -6.42 eV/atom and that of the corresponding bulk W is -8.55 eV/atom. As shown in Figure 3, the relative cohesive energy of both Mo and W initially increases rapidly with increasing the size of the nanocrystal reaching 58% and 56% of their bulk values for the two elements Mo and W respectively at $N = 2000$ atoms. On increasing the number of atoms, it exhibits a gradual increase up to the maximum value reached which was 10000 atoms.

4. CONCLUSION

In conclusion, the use of the many-body Ercok potential energy function has been extended to predict the cohesive energy of spherical metallic nanocrystals. The calculations are supported by experimental results and show reasonable consistency. The cohesive energy decreases as the nanocrystal size decreases. The dependence of the cohesive energy on the range of the potential is demonstrated as well. The model and method used in this project can be used to study the properties of nanocrystals.

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