

## THE EFFECT OF MIE-TYPE POTENTIAL RANGE ON THE COHESIVE ENERGY OF METALLIC NANOPARTICLES

T. BARAKAT<sup>\*,†</sup>, O. M. AL-DOSSARY<sup>\*</sup>  
and A. A. ALHARBI<sup>\*,†</sup>

*\*Physics Department, King Saud University  
P. O. Box 2455, Riyadh 11451, Saudi Arabia*

*†National Center for Mathematics and Physics, KACST  
P. O. Box 6086, Riyadh 11442, Saudi Arabia*

*†tbarakat@ksu.edu.sa*

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We investigate the effect of Mie-type potential range on the cohesive energy of metallic nanoparticles using the size-dependent potential parameters method. The predicted cohesive energy for different cubic structures is observed to decrease with decreasing the particle size, and increase with decreasing the range of the interatomic potential, a result which is in the right direction at least to predict the experimental values of Molybdenum and Tungsten nanoparticles.

*Keywords:* Mie-type potential; size-dependent cohesive energy; nanoparticles.

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### 1. Introduction

Traditionally, materials properties have been controlled by varying structure and composition of materials. During the last few years, a new parameter has been added, i.e., size. The fact that the materials properties change drastically when the dimension of the materials becomes comparable with the typical length scale of the phenomenon of interest, together with the ability to control the production of materials in this size range, has led to the development of nanoscience.

The nanoscience have special properties and have generated great interest in both scientific and technological communities, and the phenomenon

that nanomaterials' size-dependent cohesive energy occurs has been a topic of interest in recent years.<sup>1-3</sup>

As is well known, the cohesive energy is an important physical quantity that accounts for the bond strength of a solid, which is the energy needed to divide the solid into isolated atoms by breaking all its bonds. Cohesive energy is also a basic quantity for the thermodynamics of materials, by which we can derive almost all the thermodynamical properties of materials.<sup>4</sup>

On the other hand the cohesive energies of bulk materials are constants at a given temperature,<sup>5</sup> this is because of the small number of atoms on the surface to the volume, whereas for nanoparticles the

<sup>†</sup>Corresponding author.

cohesive energies are not constants, since the surface to volume ratio of atoms is so large, and the distance between the surface atoms and the nearest interior atoms is larger than the distance between the interior atoms, *viz* more than half of the bonds on the surface are dangling bonds and this will affect their cohesive energies.<sup>6</sup>

Among the various nanoparticles, the Molybdenum (Mo) and Tungsten (W) provoke special interest. The experimental values for the cohesive energy of these particles were reported in 2002,<sup>7</sup> and they were determined by measuring the oxidation enthalpy as a function of their sizes. Experimentally it was observed that, the cohesive energy of these nanoparticles decreases with decreasing sizes.

To explain the depression of the cohesive energy of these nanoparticles within the experimental limits, researchers have developed different models, such as the bond order-length-strength (BOLS) model,<sup>8</sup> latent heat model,<sup>9</sup> liquid drop model,<sup>10</sup> bond energy model,<sup>11</sup> the Lennard-Jones potential model,<sup>12</sup> etc. All these models can explain the depression of the cohesive energy of nanoparticles with the decreasing sizes, but the quantitative fitting to the experimental values were different.

Therefore, in the present work we will explain the depression of the cohesive energy of these nanoparticles within the experimental limit by changing the structure of these particles as function of both, their sizes and the range of the interaction potential between the interior atoms. To assess the range effects, a potential which is simple enough to comprehend the effects of any changes made to its form is considered for that reason, it is assumed that the atoms in the nanorange are interacting via Mie-type potential<sup>13</sup> and having different structures.

The importance of the nature of the interaction potential among the atoms in the nanorange will be addressed, where the effect of decreasing the range of the interaction potential is similar to the effect of decreasing the size of the nanoparticles, both will destabilize the cohesive energy.

With this in mind, this paper is organized as follows. In Sec. 2, the details of the model and the method for calculating the cohesive energy of metallic nanoparticles is discussed. In Sec. 3, the numerical results is compared with the experimental ones, and therein, remark is given to the results findings.

## 2. Model and Method

To construct the model, it is assumed that a particle in the nanometer size is taken out from any bulk crystal, where its structure is the same as the bulk crystal. For convenience, it is assumed that the nanoparticle is in cubic form, and its structure may be simple cubic (SC), body-centered cubic (BCC) or face-centered cubic (FCC). Moreover, the atoms within this nanoparticle are all in equilibrium and are interacting with each other via Mie-type potential<sup>13</sup>

$$u(r_{ij}) = \frac{\epsilon}{(m-k)} \left[ k \left( \frac{\sigma}{r_{ij}} \right)^m - m \left( \frac{\sigma}{r_{ij}} \right)^k \right], \quad (1)$$

where  $r_{ij}$  denotes the distance between atoms  $i$  and  $j$ ,  $\sigma$  denotes the equilibrium separation between the centers of any two atoms, and  $\epsilon$  is the energy located at  $\sigma$ .  $m$  and  $k$  are positive integers that account for the repulsive and attractive terms, respectively, and throughout this paper,  $m > k$  and the corresponding potential will be referred to as  $(m, k)$ .

In this model, the total energy of a nanoparticle can be determined by summing the energy of all the atoms. Minimizing the total energy with respect to the distance between the atoms, the equilibrium configuration of the nanoparticle can be obtained, and then used to calculate the cohesive energy of that particle. This procedure is just the method of this work. Accordingly, the total potential energy ( $E_n$ ) of a nanoparticle with a cubic structure having  $n$  atoms is given by

$$E_n = \frac{1}{2} \sum_{i=1}^n \sum_{\substack{j=1 \\ j \neq i}}^n u(r_{ij}). \quad (2)$$

Inserting Eq. (1) into Eq. (2);

$$E_n = \frac{n\epsilon}{2(m-k)} \left[ k \left( \frac{\sigma}{R} \right)^m A_m - m \left( \frac{\sigma}{R} \right)^k A_k \right], \quad (3)$$

where

$$A_m = \frac{1}{n} \sum_{i=1}^n \sum_{\substack{j=1 \\ j \neq i}}^n \left( \frac{1}{a_{ij}} \right)^m \quad \text{and} \quad A_k = \frac{1}{n} \sum_{i=1}^n \sum_{\substack{j=1 \\ j \neq i}}^n \left( \frac{1}{a_{ij}} \right)^k \quad (4)$$

are the potential parameters with  $a_{ij} = r_{ij}/R$ , and  $R$  is the nearest distance between two atoms. It is obvious that the potential parameters  $A_m$  and

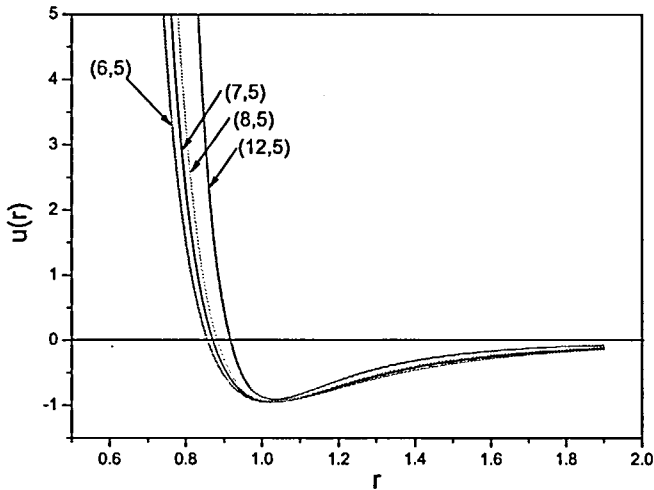


Fig. 1. Mie-type potential showing different ranges for different values of  $m$  and fixed  $k$ .

$A_k$  are related to the particle size  $n$ ; related to the structure of the nanoparticle through  $a_{ij}$ , and highly dependent on the potential values  $m$ , and  $k$ . That is to say, changing the the values of  $m$  and  $k$  means changing the range of Mie potential. Figure 1 shows that fixing the value of  $k$ , and decreasing the values of  $m$  will increase the range of the potential and soften the repulsive wall.

On the other hand, in equilibrium the total potential energy of a nanoparticle should be minimum, that is  $\frac{dE_n}{dR}|_{R_0} = 0$ , which will give

$$R_0 = \sigma \left( \frac{A_m}{A_k} \right)^{\frac{1}{m-k}}, \quad (5)$$

where  $R_0$  is the nearest distance between two atoms in equilibrium. Inserting Eq. (5) into Eq. (3), the total energy of a nanoparticle in equilibrium configuration is given by

$$E_n = -\frac{n \varepsilon}{2} \left( \frac{A_k^{\frac{m}{m-k}}}{A_m^{\frac{k}{m-k}}} \right). \quad (6)$$

Apparently,  $E_n$  is the cohesive energy of  $n$  atoms, and the cohesive energy per atom  $E_a$  is

$$E_a = -\frac{\varepsilon}{2} \left( \frac{A_k^{\frac{m}{m-k}}}{A_m^{\frac{k}{m-k}}} \right). \quad (7)$$

Equation (7) is similar to the expression of the cohesive energy of bulk materials, and the potential parameters  $A_m$  and  $A_k$  depend only on the particle size for fixed values of  $m$  and  $k$ , whereas, these parameters are size independent for bulk

materials.<sup>14</sup> For SC, BCC, and FCC structures, the variations of  $A_m$  and  $A_k$  with the particle size for different values of  $m$ , and  $k$  are shown in Figs. 2–7, in which the solid-symbol lines are obtained by means of Eq. (4). From these figures it is clear that both  $A_m$  and  $A_k$  increase with increasing the size of the particle, and they are converging rapidly to the corresponding bulk values when the repulsive part of the potential becomes larger.

To make the cohesive energy free from the parameter  $\varepsilon$ , the relative cohesive energy of a nanoparticle with respect to the cohesive energy of the corresponding bulk material is calculated.

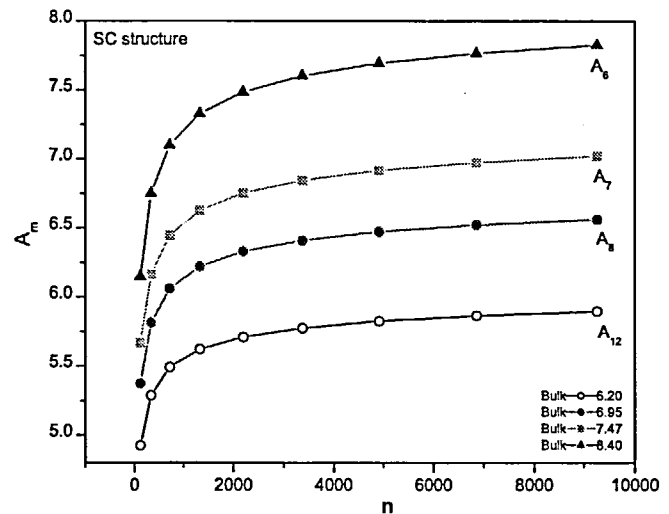


Fig. 2. Size-dependent potential parameters  $A_m$  of simple cubic structure as a function of nanoparticle size  $n$ .

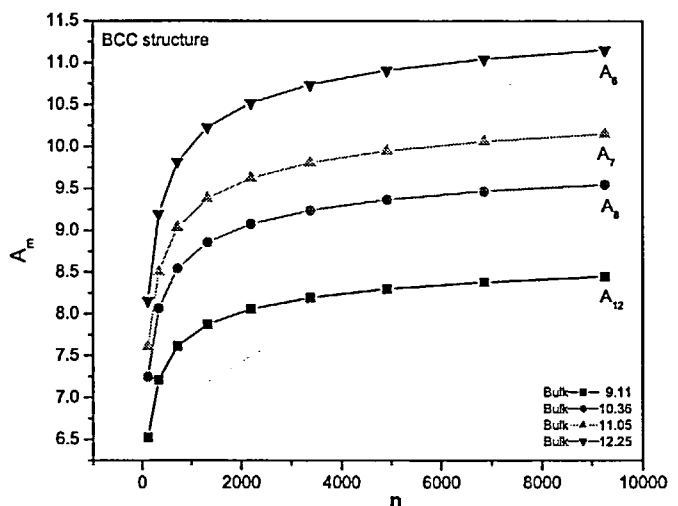


Fig. 3. Size-dependent potential parameters  $A_m$  of body-centered cubic structure as a function of nanoparticle size  $n$ .

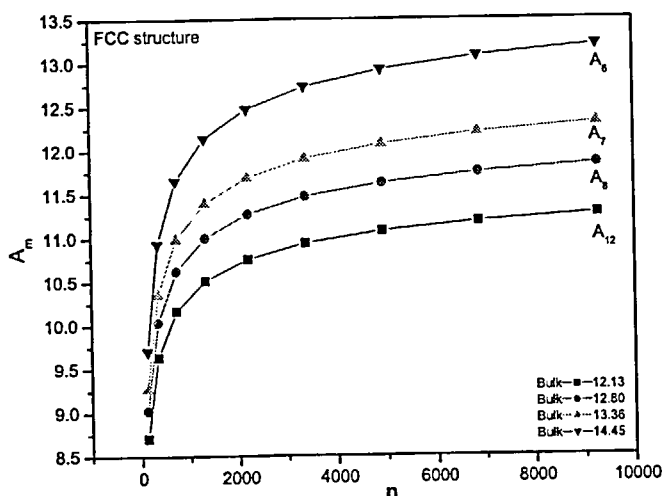


Fig. 4. Size-dependent potential parameters  $A_m$  of face-centered cubic structure as a function of nanoparticle size  $n$ .

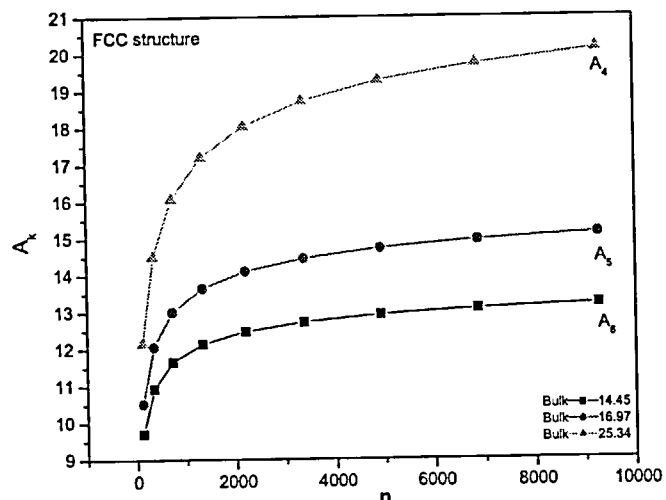


Fig. 7. Size-dependent potential parameters  $A_k$  of face-centered cubic structure as a function of nanoparticle size  $n$ .

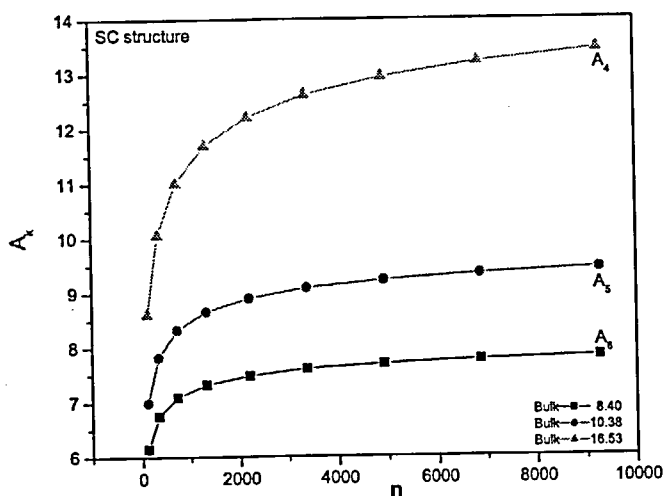


Fig. 5. Size-dependent potential parameters  $A_k$  of simple cubic structure as a function of nanoparticle size  $n$ .

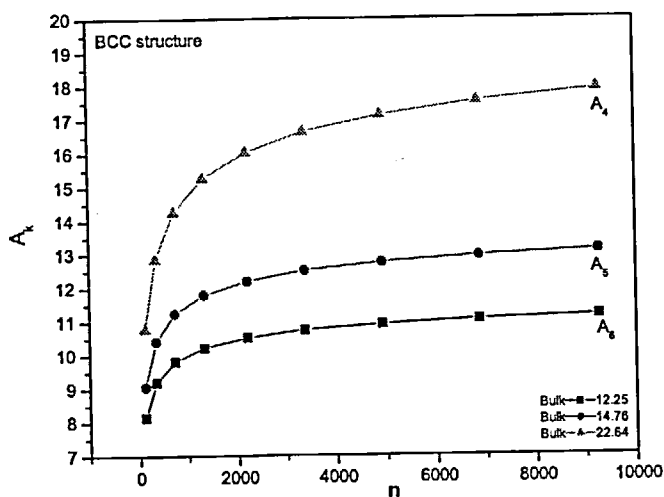


Fig. 6. Size-dependent potential parameters  $A_k$  of body-centered cubic structure as a function of nanoparticle size  $n$ .

Therefore, if the cohesive energy of bulk material is  $E_0$ , then

$$\frac{E_a}{E_0} = \frac{P_0}{2} \left( \frac{A_k^{\frac{m}{m-k}}}{A_m^{\frac{k}{m-k}}} \right), \quad (8)$$

where  $P_0 = 2 \left( \hat{A}_m^{\frac{k}{m-k}} / \hat{A}_k^{\frac{m}{m-k}} \right)$ ,  $\hat{A}_m$  and  $\hat{A}_k$  are the corresponding potential parameters of bulk materials. An explicit list of calculations for the lattice sums  $\hat{A}_m$  and  $\hat{A}_k$  for the three cubic Bravais lattices for different values of  $m$  and  $k$  with large  $n$  are given in Table 1, so that the reader may, if so inclined, reproduce the results.

Table 1. The lattice sums  $\hat{A}_m$  or  $\hat{A}_k$  for the three cubic Bravais lattices for different values of  $m$  and  $k$  with large  $n$ .

m or k	$\hat{A}_m$ or $\hat{A}_k$		
	Simple cubic	Body-centered cubic	Face-centered cubic
$\leq 3$	$\infty$	$\infty$	$\infty$
4	16.53	22.64	25.34
5	10.38	14.76	16.97
6	8.40	12.25	14.45
7	7.47	11.05	13.36
8	6.95	10.36	12.80
9	6.63	9.89	12.49
10	6.43	9.56	12.31
11	6.29	9.31	12.20
12	6.20	9.11	12.13

### 3. Numerical Results and Discussion

The effects of the size-dependent potential parameters model on the relative cohesive energy of metallic nanoparticles with different sizes; different structures, and with different potential ranges are shown in Figs. 8-11. In these figures the solid-symbol lines are the results calculated by means of Eq. (8), and those lines with the star symbols are denoted to the experimental values of Mo and W.<sup>7</sup>

From Figs. 8-11, it can be seen that the relative cohesive energy of the nanoparticles depends

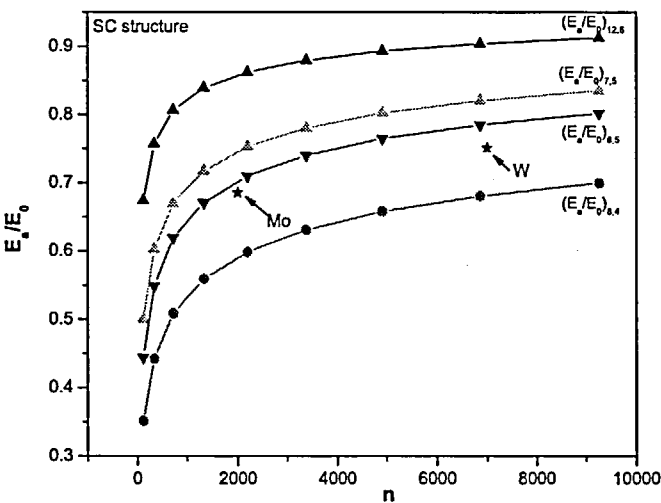


Fig. 8. The particle size dependence of the relative cohesive energy of simple cubic nanoparticles with different potential ranges, where the star symbols denote the experimental values.<sup>7</sup>

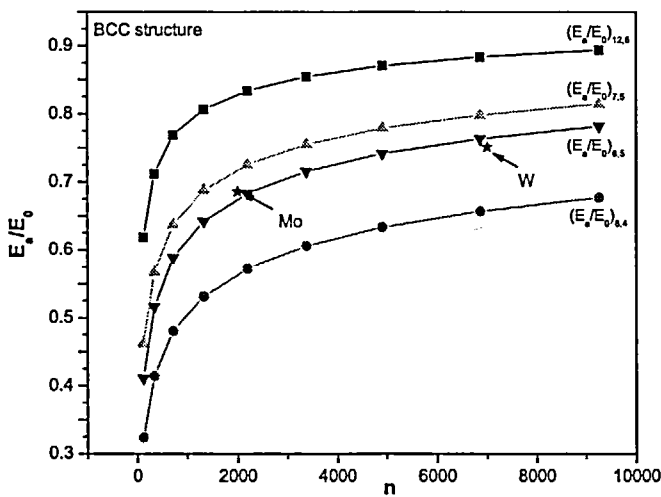


Fig. 9. The particle size dependence of the relative cohesive energy of body-centered cubic nanoparticles with different potential ranges, where the star symbols denote the experimental values.<sup>7</sup>

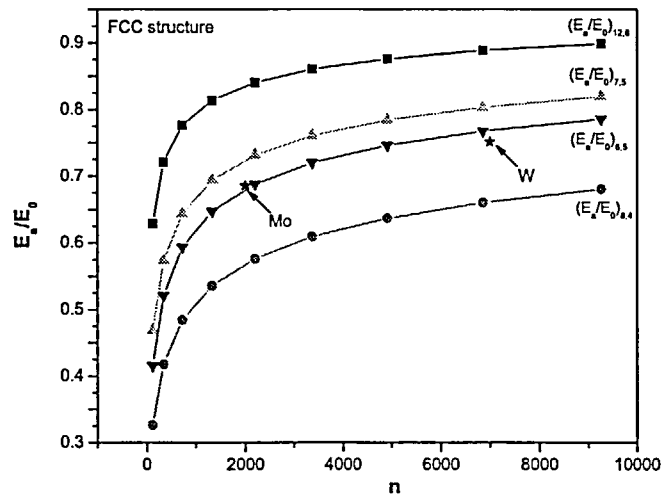


Fig. 10. The particle size dependence of the relative cohesive energy of face-centered cubic nanoparticles with different potential ranges, where the star symbols denote the experimental values.<sup>7</sup>

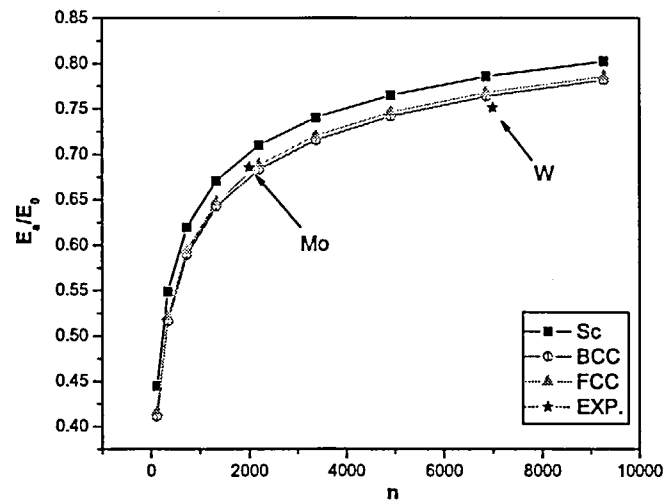


Fig. 11. The particle size dependence of the relative cohesive energy of different structures with Mie potential (6, 5), where the star symbols denote the experimental values.<sup>7</sup>

on the particle size, i.e., the relative cohesive energy of a nanoparticle increases when the particle size is increased, and approaches to that of the corresponding bulk metal when  $n$  is too large. It is also shown that, the relative cohesive energy of the nanoparticles depends on the range of the potential, where it is observed that the relative cohesive energy of Mo and W nanoparticles are bounded respectively from top by (12, 6), and from bottom by (8, 4) Mie-type potentials. The effect of decreasing the range of the interaction potential is similar to the effect of decreasing the size of the nanoparticles, both are destabilizing the

cohesive energies. Consequently, a systematic search in between has been performed in order to find the possible potential which will predict the experimental values for the cohesive energy of Mo and W nanoparticles. It is observed that the Mie interaction potential with  $m = 6$ , and  $k = 5$  can be a possible candidate to predict the cohesive energy of Mo and W nanoparticles.

The predicted results of (6, 5) Mie-type potential used for SC, BCC, and FCC nanoparticles shown in Fig. 11 are the most closest ones to the experimental values. Furthermore, it is also shown that the size, range, and shape effects on the cohesive energy are more obvious for SC nanoparticles structure than those for BCC and FCC structures.

In conclusion, this work demonstrates the dependence of the cohesive energy of metallic nanoparticles on the range of the potential used to model atom-atom interactions, and also its dependence on the sizes and the structural of the metallic nanoparticles. The present results for the cohesive energy of Mo and W nanoparticles are consistent with the corresponding experimental values, where it is reported that the cohesive energy of Mo nanoparticle with size  $n = 2000$  is  $-410$  kJ/mol,<sup>7</sup> and the cohesive energy of bulk Mo is  $-598$  kJ/mol.<sup>15</sup> Whereas, the cohesive energy for the W nanoparticle with size  $n = 7000$  is  $-619$  kJ/mol,<sup>7</sup> and the cohesive energy of bulk W is  $-824$  kJ/mol.<sup>15</sup> These results suggest that the Mie interaction potential with  $m = 6$ , and  $k = 5$  can be a possible candidate to study the properties of different nanoparticles by considering the size-dependent potential parameters.

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