An investigation of the size-dependent cohesive energy and the structural stability of spherical metallic nanoparticles

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Abstract

The size-dependent potential parameters method is used to investigate the effect of many-body interactions on the structural stabilities and the cohesive energy of molybdenum (Mo) and tungsten (W) spherical metallic nanoparticles. The total interaction energy is represented in terms of a two-body Mie-type potential plus a three-body Axilord–Teller-type potential. Results emphasized the importance of multi-body forces to explain nano-structures. The predicted cohesive energy for these nanoparticles is observed to decrease with decreasing sizes, a result which is in agreement with experimental results.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

In the last few years an increased interest in nano-systems has revealed a new realm of physical phenomena. This special interest in nano-systems comes from the fact that at the nanometre level the physical properties of these objects not only depend on their structure, but also their size. Since this was realized, the size-dependent cohesive energy phenomenon has been a topic of interest [1–3].

Currently, the cohesive energy is considered as one of the most fundamental thermal properties that describes the inner structural energy of nanoparticles and shows how strongly atoms hold together. It is regarded as being directly related to the nature of the thermal stability of the nanoparticle. It also plays an important role in the melting phenomenon [4–6].

Among the various nanoparticles, the molybdenum (Mo) and tungsten (W) provoke special interest. The experimental measurements in 2002 [7] for the cohesive energy of the Mo and the W nanoparticles as a function of their sizes, have placed the study of the size-dependent cohesive energy of nanoparticles on a new footing. It was observed that the cohesive energy of nanoparticles decreases with decreasing size.

So far, a lot of efforts have been made to explain the cohesive energy depression of these nanoparticles within experimental limits. Researchers have developed different models, such as the bond order-length-strength (BOLS) model [8], latent heat model [9], liquid drop model [10], bond energy model [11], the Lennard–Jones potential model [12], etc. All these models can explain the depression of the cohesive energy of nanoparticles with their decreasing size, but the quantitative fitting to the experimental values is different.

Recently we have proposed a size-dependent potential parameters (SDPP) model and applied it to investigate the two-body interaction (Mie-type) potential range on the cohesive energy of metallic nanoparticles [13]. Encouraged by its satisfactory performance through comparisons with other models, we feel tempted to extend the SDPP model to investigate the cohesive energy of metallic nanoparticles by using this time an empirical many-body potential energy function (PEF).

This model is very easy to implement and the results are sufficiently accurate for practical purposes. Moreover, the SDPP model can provide detailed insights into the physics of these particles when seeking to clarify the dependence of their thermodynamic behaviours on their sizes. The benefits

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of the SDPP approach become increasingly apparent as the characteristic size of the system decreases.

With this in mind, this paper is organized as follows. In section 2, the model and method for calculating the cohesive energy of spherical metallic nanoparticles are discussed. In section 3, the numerical results of this work compared with the experimental ones are presented, and therein, we remark on the results and our findings.

2. Model and method of calculations

To construct the SDPP model, we assume that a spherical metallic nanoparticle in the nanometre size is generated from ideal BCC or FCC 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-neighbour distance is considered as the radius of the first shell and the second nearest-neighbour distance as the radius of the second shell, and so on. The number of shells in the nanoparticle, the radius of the nanoparticle, the number of atoms in each shell and the total number of atoms (n) in the nanoparticle can all be easily obtained. We assume that in the absence of external forces a function $E_n(\vec{r_1}, \ldots, \vec{r_N})$ for a system of n atoms exists to describe their potential energy as a function of their positions which may be expanded as [14]

$$E_n = \frac{1}{2} \sum_{\substack{i \\ i \neq j}}^{n} \sum_{j}^{n} u_2(\vec{r_i}, \vec{r_j})$$
$$+ \frac{1}{6} \sum_{\substack{i \\ i \neq j \neq k}}^{n} \sum_{j}^{n} \sum_{k}^{n} u_3(\vec{r_i}, \vec{r_j}, \vec{r_k}) + \cdots, \qquad (1)$$

where, $u_2(\vec{r_i}, \vec{r_j})$ and $u_3(\vec{r_i}, \vec{r_j}, \vec{r_k})$ denote two-body and three-body interactions, respectively. This is the so-called many-body expansion of E_n, and it is usually believed that the series has a quick convergence, and therefore, the higher moments may be neglected. In this work, the two-body interactions are assumed to be given by a Mie-type potential [15]:

$$u_2(\vec{r_i}, \vec{r_j}) = \varepsilon \left[\left(\frac{r_0}{r_{ij}} \right)^8 - 2 \left(\frac{r_0}{r_{ij}} \right)^4 \right], \qquad (2)$$

where r_{ij} denotes the distance between atoms i and j, r_0 denotes the equilibrium separation between the centres of any two atoms, and ε is the two-body energy at $r_{ij} = r_0$. The three-body term is represented by an Axilord–Teller-type triple dipole function [16]

$$u_3(\vec{r_i}, \vec{r_j}, \vec{r_k}) = \frac{z(1 + 3 \cos \theta_i \cos \theta_j \cos \theta_k)}{(r_{ij} r_{ik} r_{jk})^3}, \qquad (3)$$

where $\theta_i, \theta_j, \theta_k$ and r_{ij}, r_{ik}, r_{jk} represent the angles and the sides of the triangle formed by the three particles i, j and k, respectively. The parameter z is the intensity of the three-body interactions.

In this model, the total energy of a nanoparticle can be determined by summing the energy of all the atoms.
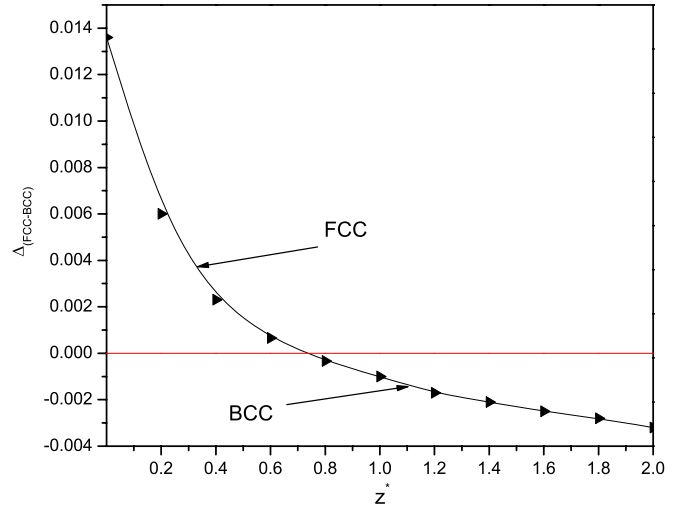

Figure 1. Relative minimum energy difference as a function of z^* between FCC and BCC structures; $z^* \geqslant 0.70$ BCC is more stable.

Therefore, combining equations (1)–(3), we can write the effective cohesive energy per atom E_a^* of a spherical metallic nanoparticle with a cubic internal structure as

$$E_a^* = \frac{1}{2} A_8 r^{*8} - A_4 r^{*4} + z^* T_h r^{*9}, \qquad (4)$$

where $E_a^* = E_n/(n\varepsilon)$, $z^* = z/(\varepsilon r_0^9)$, $r^* = r_0/d$, and d represents the nearest-neighbour distance in the crystal. The coefficients A_8, A_4 and T_h are lattice sums and they are given by

$$A_8 = \frac{1}{n} \sum_{\substack{i \\ i \neq j}}^{n} \sum_{j}^{n} \left(\frac{d}{r_{ij}} \right)^8, \qquad A_4 = \frac{1}{n} \sum_{\substack{i \\ i \neq j}}^{n} \sum_{j}^{n} \left(\frac{d}{r_{ij}} \right)^4, \qquad (5)$$

and

$$T_h = \frac{1}{6n} \sum_{\substack{i \\ i \neq j \neq k}}^{n} \sum_{j}^{n} \sum_{k}^{n} \frac{(1 + 3 \cos \theta_i \cos \theta_j \cos \theta_k)}{\left(\frac{r_{ij}}{d} \frac{r_{ik}}{d} \frac{r_{jk}}{d} \right)^3}. \qquad (6)$$

It is obvious that the potential parameters A_8, A_4 and T_h are related to the particle size, and related to the structure of the nanoparticle through d, and highly dependent on the potential powers. That is to say, changing the potential powers means changing the range of the potential.

The stability condition for the minimum energy configuration of a nanoparticle at $T = 0°$ K can be obtained by considering $\partial E_n/\partial V = 0$ or $\partial E_a^*/\partial d = 0$. This is because the atomic volume V is related to d by $V = N_0 g d^3$, where N_0 denotes Avagadro's number, and g is a geometrical constant. Thus the stability condition becomes

$$A_8 r^{*8} - A_4 r^{*4} + \frac{9}{4} z^* T_h r^{*9} = 0. \qquad (7)$$

Evidently, equation (4) is similar to the expression of the cohesive energy for bulk materials. On the other hand, the effect of the three-body interaction term on the cohesive energy for bulk materials is accomplished by varying z^* between
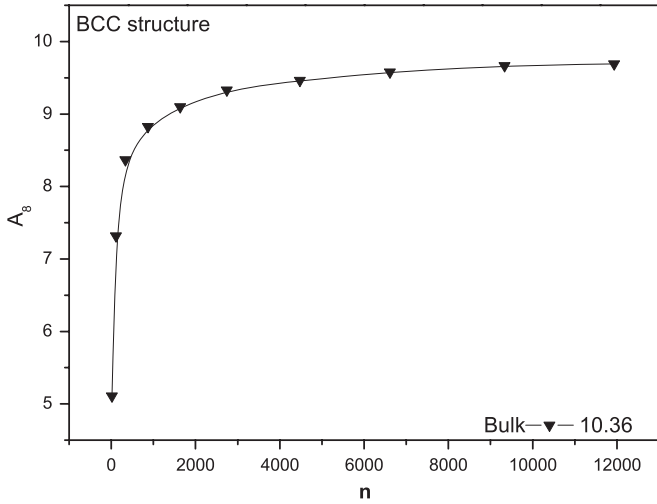
Figure 2. Size-dependent potential parameters A_8 of a body-centred cubic structure as a function of nanoparticle size n.
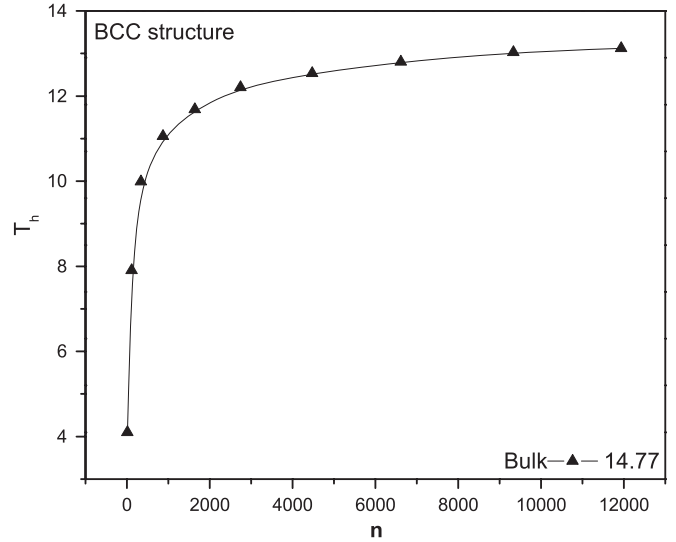

Figure 4. Size-dependent potential parameters T_h of body-centred cubic structure as a function of a nanoparticle of size n.
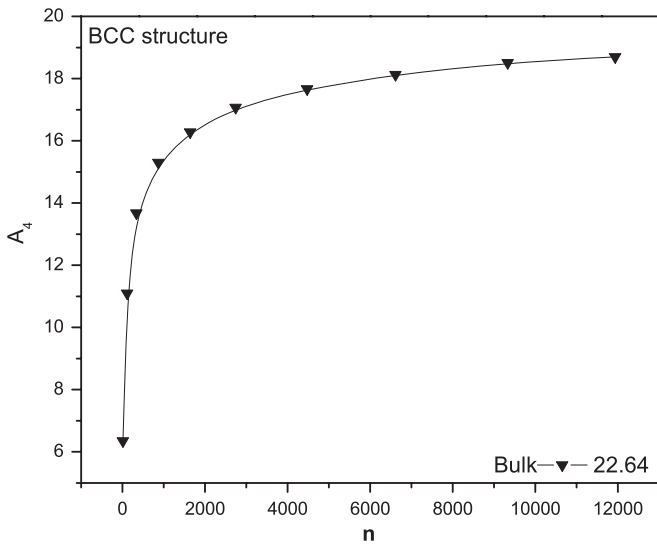

Figure 3. Size-dependent potential parameters A_4 of a body-centered cubic structure as a function of a nanoparticle of size n.
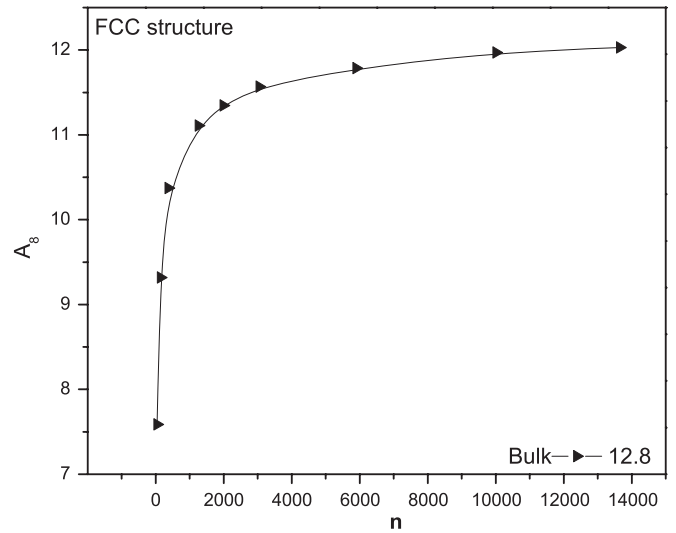

Figure 5. Size-dependent potential parameters A_8 of face-centred cubic structure as a function of a nanoparticle of size n.

0.0 and 2.0 in increments of 0.2. Therefore, first r^* values for BCC and FCC bulk structures were calculated from the stability condition as a function of z^*. The potential parameters A_8, A_4 and T_h for bulk structures are used at this stage [13, 17]. The positive real root of equation (7) is assumed as an acceptable solution. The minimum cohesive energies per atom E_a^* for BCC and FCC crystalline structures were calculated as a function of z^*. Furthermore, in figure 1 the relative energy differences, $\Delta_{(\text{FCC}-\text{BCC})} = (E_{a\,(\text{FCC})}^* - E_{a\,(\text{BCC})}^*)/E_{a\,(\text{FCC})}^*$ is plotted as a function of z^* to demonstrate the corresponding stability regions. Apparently, for this particular case, the FCC structure is energetically more favourable for $0.3 \leqslant z^* \leqslant 0.7$, and for $0.7 \leqslant z^*$ the BCC structure was found to be more stable. However, from figure 1 it is clear that the variation of the minimum energy induced by the crystalline structure difference between BCC and FCC is fairly small and may lead to phase transition at small sizes. Therefore, we calculate

the minimum energy for both BCC and FCC structures at $z^* = 0.70$ and $z^* = 1.20$.

On the other hand, in the nano-range, the potential parameters A_8, A_4 and T_h in equations (5) and (6) depend on the particle size n, and the investigation was carried out again for BCC and FCC structures with R_{cut} varying shell by shell around one central atom. For each value of R_{cut} a new nanoparticle size was generated. The variations of A_8, A_4 and T_h with the particle size are reproduced and are shown in figures 2–7, where the solid-symbol lines are the results calculated by equations (5) and (6). From these figures it is clear that A_8, A_4 and T_h increase with increasing size of the particle, and converges rapidly to the corresponding bulk values.

For every generated spherical metallic nanoparticle of structure BCC or FCC, r^* was calculated from the stability
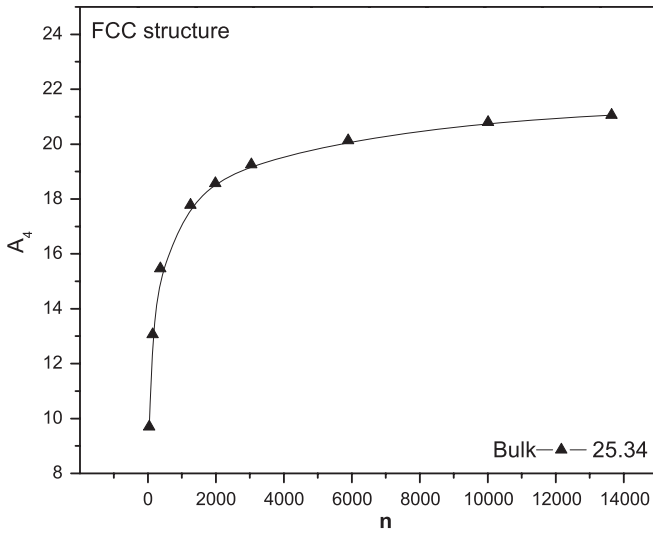
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Figure 6. Size-dependent potential parameters A_4 of face-centred cubic structure as a function of a nanoparticle of size n.
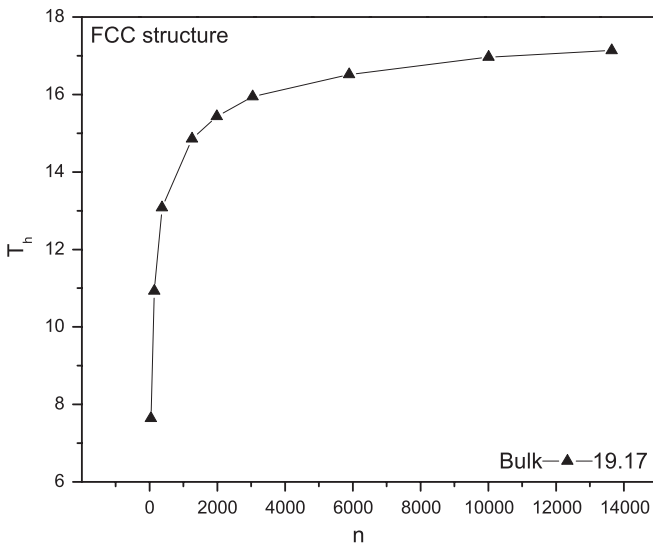

Figure 7. Size-dependent potential parameters T_h of a face-centred cubic structure as a function of a nanoparticle of size n.
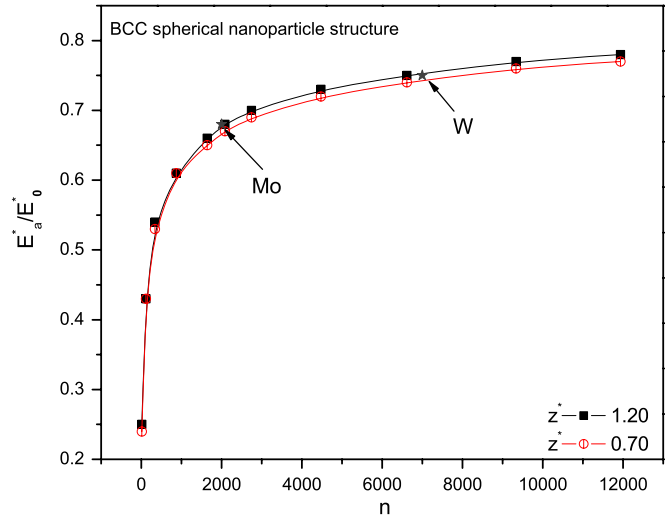

Figure 8. The particle size dependence of the relative cohesive energy of BCC spherical nanoparticles. The star symbols denote the experimental values [7].
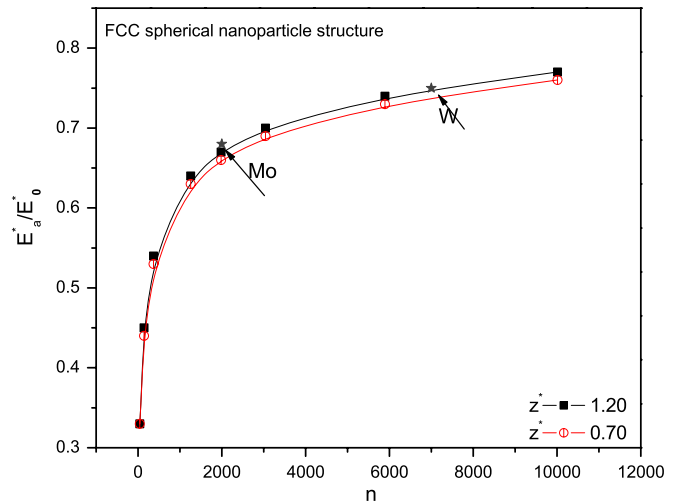

Figure 9. The particle size dependence of the relative cohesive energy of FCC spherical nanoparticles. The star symbols denote the experimental values [7].

condition at $z^* = 0.70$ and $z^* = 1.20$. The positive real root of equation (7) is assumed as an acceptable solution. The minimum cohesive energy per atom E_a^* for BCC and FCC spherical metallic nanoparticles was calculated as a function of n.

Typically, to make the minimum cohesive energy free from the parameter ε, we calculate the relative minimum cohesive energy of a nanoparticle with respect to the cohesive energy of the corresponding bulk material, i.e. E_a^*/E_0^*, where we denote the cohesive energy of the bulk material by E_0^*. The results of the SDPP model for the relative cohesive energy of our spherical metallic nanoparticles with different sizes and different structures are shown in figures 8 and 9. In these figures the solid-symbol lines are the results calculated

by equation (7), and those with the star symbols denote the experimental values of Mo and W nanoparticles [7].

3. Numerical results and discussion

As was mentioned before, the only available experimental values are the cohesive energies of Mo and W nanoparticles, appeared in the literature [7, 18]. It is reported that the cohesive energy of the Mo nanoparticle of 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 nanoparticle of size $n = 7000$, its cohesive energy is -6.42 eV/atom, and that of the corresponding bulk W is -8.55 eV/atom.

From figures 8 and 9 it can be seen that the relative cohesive energy of the nanoparticles depends on the particle

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size, i.e. the relative cohesive energy of a nanoparticle increases when the particle size is increased, and approaches that of the corresponding bulk metal when n is very large. It is also shown that the relative cohesive energy of the nanoparticles depends on the intensity of the three-body interaction z^*, as a result of its dependence on the stability of the crystal, where it is observed that the relative cohesive energy of the present work for both the Mo and W nanoparticles are reproduced at the values $z^* = 0.70$ and $z^* = 1.20$. This result supported the phase transition idea [19, 20], that is metals with BCC structure would have a FCC structure when the crystal size is small enough.

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 structure of the metallic nanoparticles. The present results are consistent with the corresponding experimental values for the cohesive energy of Mo and W nanoparticles, and suggests that the two-body Mie-type potential plus a three-body Axilord–Teller-type potential can be a possible candidate to study the properties of various metallic nanoparticles by considering the size-dependent potential parameters model.

Acknowledgments

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