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Calculation of the cohesive energy of metallic nanoparticles by the Lennard–Jones potential

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Abstract

The cohesive energy of metallic nanoparticles has been studied by Lennard–Jones potential. It is found that the Lennard–Jones potential can be used to calculate the cohesive energy of metallic nanoparticles by considering the size-dependent potential parameters. It is predicted that the cohesive energy of small particles decreases with decreasing the particle size, which is consistent with the experimental values of Mo and W nanoparticles.

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Keywords: Lennard–Jones potential; Cohesive energy; Nanoparticles

It is shown that the thermodynamic properties of nanoparticle depend on the particle size [1–8]. However, in all the properties, only the melting point has been measured experimentally [2,3]. Up to last year, the first experimental data on cohesive energy of Mo and W nanoparticles have been determined through measuring the oxidation enthalpy of the nanoparticles [8].

In our previous work [7], a very simple model has been developed accounting for the size-dependent cohesive energy of nanoparticles. In that model, we assume that the cohesive energy equals to the energy to destroy the metallic bonds, where the concept of the metallic bond is adopted from the concept of ionic bond by considering the nearest coordination number. By taking the coordination number difference between the surface atoms and the inside atoms into consideration, we obtained a simple relation for the cohesive energy of nanoparticle, and which give the predictions on cohesive energy of Mo and W nanoparticles agreeing with the corresponding experimental results. However, in that simple model, the structural difference (e.g. the difference between the simple cubic and the face-centered cubic) is not considered.

To overcome the deficiency, we can refer to the interaction potential functions. If the energy of each atom in a nanoparticle is known, the total energy of the nanoparticle can be obtained by summing all the energy of each atom. Minimizing the total energy with respect to the distance between atoms, we can get the equilibrium configuration of the nanoparticle, and then we can calculate the cohesive energy of nanoparticles. This procedure is just the method of this work. In the present calculation, we assume that the atoms interact via Lennard–Jones potential

$$u(r_{ij}) = 4\varepsilon\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right] \tag{1}$$

where r_{ij} is the distance between the atom i and the atom j, and ε and σ are the parameters . Empirical potential of this type, originally developed for description of inert gases, and now is commonly used to study the properties of condensed systems [9].

It is needed to construct a nanoparticle model to start our work. In the present work, we assume that the nanoparticle can be formed in this way: first, a particle in nanometer size is taken out from the bulk crystal, where its structure is the

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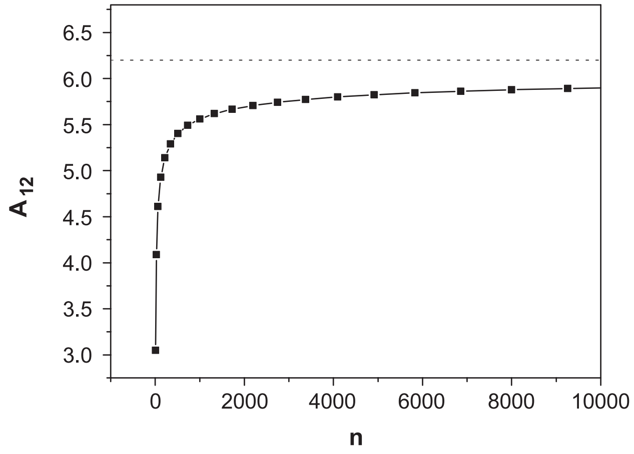

Fig. 1. Potential parameter A_{12} of simple cubic structure as a function of particle size *n*.

same as the bulk crystal; second, the atoms of the particle interact with each other; third, in equilibrium, the nanoparticle is formed. For convenience, we assume the nanoparticle is in cubic form, and its structure may be simple cubic structure (SC), face-centered cubic (FCC) or body-centered cubic (BCC). The close-packed hexagonal (cph) structure has the same density and coordination number as the FCC structure, so they are identical in our present calculation.

The potential energy (E) of the cubic nanoparticle with n atoms can be written as

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

Inserting Eq. (1) into Eq. (2), we have

$$E=2\varepsilon\cdot n\cdot\left[A_{12}\left(\frac{\sigma}{R}\right)^{12}-A_{6}\left(\frac{\sigma}{R}\right)^{6}\right] \tag{3}$$

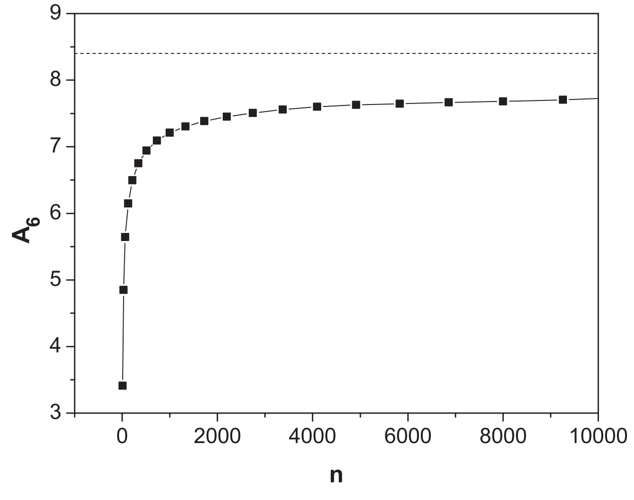

Fig. 2. Potential parameter A_6 of simple cubic structure as a function of particle size *n*.

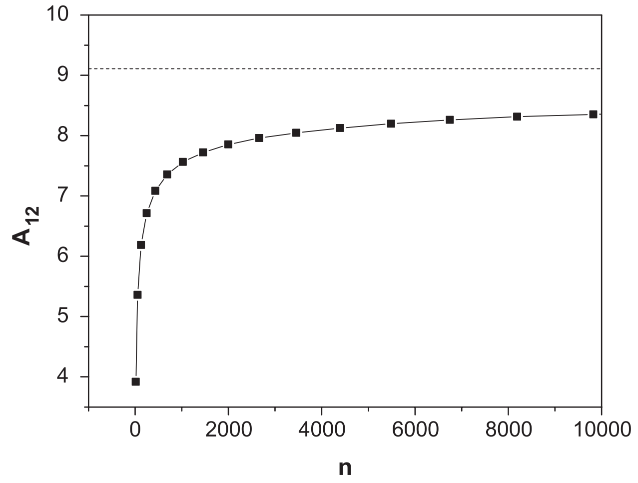

Fig. 3. Potential parameter A_{12} of body-centered cubic structure as a function of particle size *n*.

where

$$A_{12}=\frac{1}{n}\sum_{i=1}^{n}\sum_{\substack{j=1\\ j\neq i}}^{n}\left(\frac{1}{a_{ij}}\right)^{12},\ A_{6}=\frac{1}{n}\sum_{i=1}^{n}\sum_{\substack{j=1\\ j\neq i}}^{n}\left(\frac{1}{a_{ij}}\right)^{6} \tag{4}$$

where we have taken $r_{ij}=a_{ij}R$, and R is the nearest distance between two atoms. It is obvious that A_{12} and A_6 are related to the particle size n. If the number of atom n is fixed, A_{12} and A_6 are constants. In equilibrium, the total potential energy is minimum, i.e., $\mathrm{d}E/\mathrm{d}R=0$, which gives

$$R_0=\left(\frac{2A_{12}}{A_6}\right)^{\frac{1}{6}}\cdot\sigma \tag{5}$$

where R_0 is the nearest distance between two atoms in equilibrium. Inserting Eq. (5) into Eq. (3), we can get

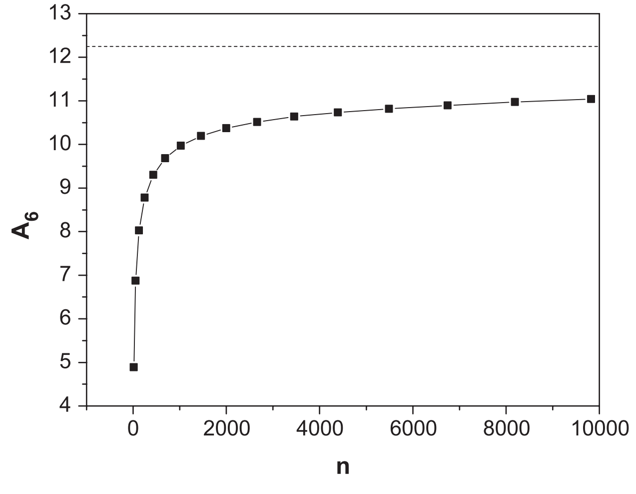

Fig. 4. Potential parameter A_6 of body-centered cubic structure as a function of particle size *n*.

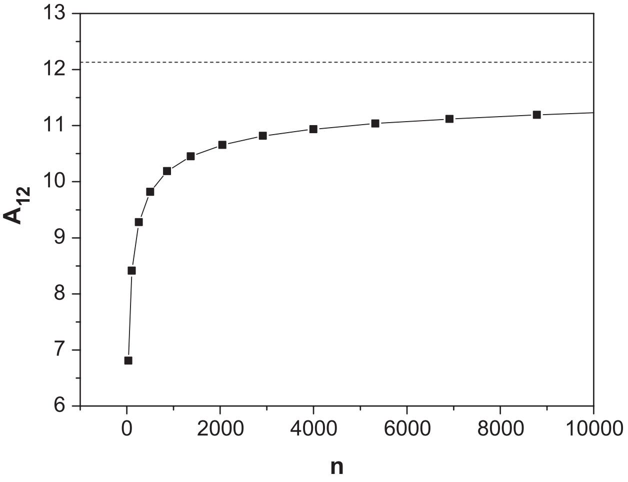

Fig. 5. Potential parameter A_{12} of face-centered cubic structure as a function of particle size n.

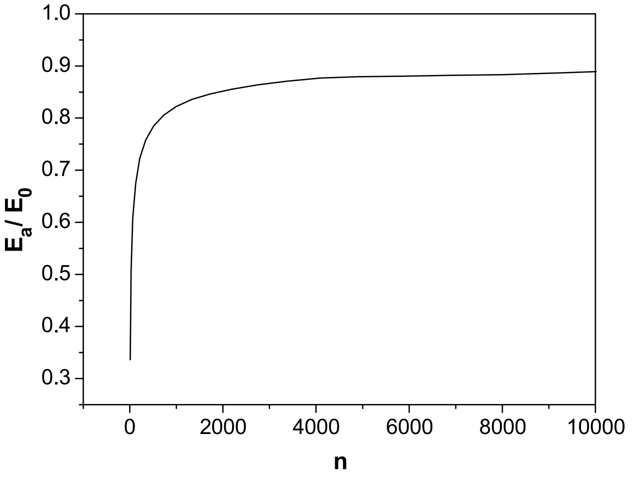

Fig. 7. The particle size dependence of the cohesive energy of simple cubic nanoparticles.

the total energy E_n in equilibrium configuration, which is

$$E_n = -\frac{A_6^2}{2A_{12}} \cdot n \cdot \varepsilon \tag{6}$$

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

$$E_a = -\frac{A_6^2}{2A_{12}} \cdot \varepsilon \tag{7}$$

Eq. (7) is similar to the expression of the cohesive energy of bulk materials. However, in Eq. (7), the parameters A_{12} and A_6 depend on the particle size, where these parameters of bulk materials are independent of the size of bulk materials [10]. For cubic structures, the variations of A_{12} and A_6 with the increasing the particle size are shown in Figs. 1–6, where the solid-symbol lines are the results calculated by Eq. (4), and the dash lines denote the corresponding values of bulk materials [10]. It is shown that both A_{12} and A_6 increase with increasing the particle size, and approach to the corresponding bulk values when the particle size becomes larger.

In Eq. (7), the size-dependent factor is $A_6^2/2A_{12}$, and the parameter å can be determined by fitting the cohesive energy of bulk crystals. For simplicity, we can calculate the relative cohesive energy of nanoparticles to make the cohesive energy free of the parameter ε. If E_0 denotes the cohesive energy of bulk metals, we have

$$\frac{E_a}{E_0} = P_0 \cdot \frac{A_6^2}{2A_{12}} \tag{8}$$

where $P_0 = 2A'_{12}/A'^2_6$, A'_{12} and A'_6 are the corresponding parameters of bulk metals. For three different structures SC, BCC and FCC of nanoparticles, the values of P_0 are 0.176, 0.121 and 0.116, respectively [10].

The calculated results on the cohesive energy of metallic nanoparticles with different structures are shown in Figs. 7–9, where the solid lines are the present calculation results

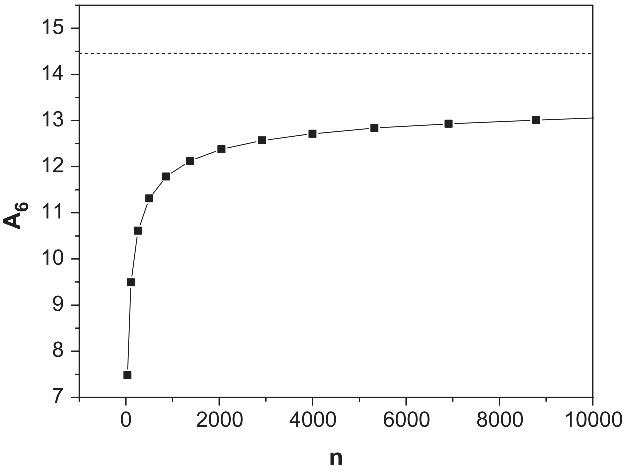

Fig. 6. Potential parameter A_6 of face-centered cubic structure as a function of particle size n.

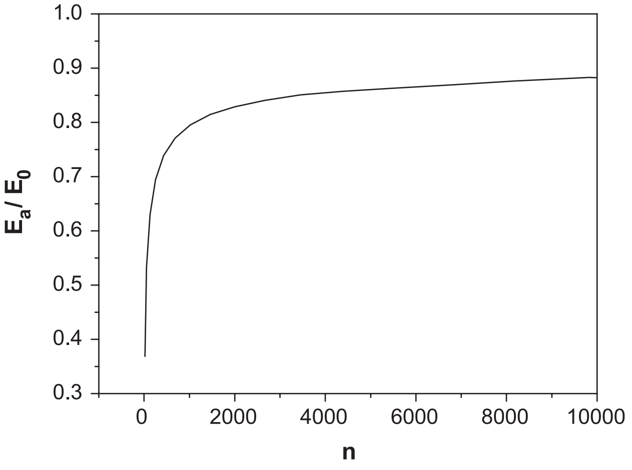

Fig. 8. The particle size dependence of the cohesive energy of body centered cubic nanoparticles.

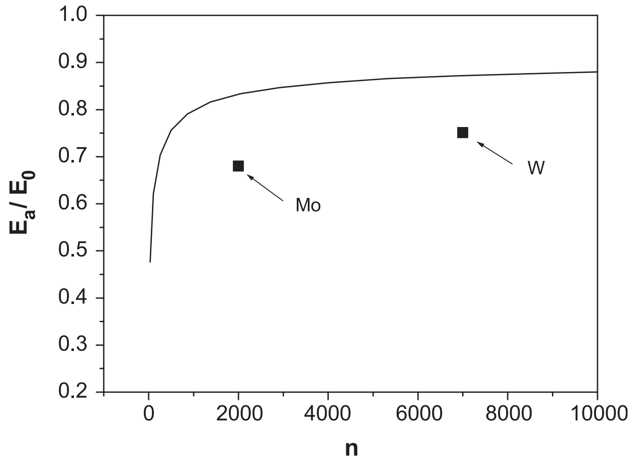

Fig. 9. The particle size dependence of the cohesive energy of face-centered cubic nanoparticles, where the square symbols denote the experimental values [8].

calculated by Eq. (8). Since the cohesive energy of nanoparticles is difficult to be measured, the experimental values on the cohesive energy of Mo and W nanoparticles appeared in literature up to last year [8], where the values are obtained by measuring the oxidation enthalpy of the nanoparticles. It is reported that the cohesive energy of Mo nanoparticles in the size $n = 2000$ is -410 kJ/mol [8], where the cohesive energy of bulk Mo is -598 kJ/mol [11]. For the W nanoparticles in the size $n = 7000$, their cohesive energy is -619 kJ/mol [8] and that of the corresponding bulk W is -824 kJ/mol [11]. As a comparison with our present theoretical prediction, the normalized experimental values on the cohesive energy of Mo and W nanoparticles in FCC structure are also shown in Fig. 9.

It is shown that the cohesive energy of the nanoparticles depends on the particle size, i.e. the relative cohesive energy of nanoparticles increases with increasing the particle size, and approaches to that of the corresponding bulk metal. The present calculation values on cohesive energy of Mo and W nanoparticles are higher than the corresponding experimental ones. However, considering the assumptions in our model that all the atoms of the nanoparticle have the same variation in equilibrium and the nanoparticle is in cubic form, the present results are acceptable.

As mentioned in the beginning of this letter, the structural difference is considered presently. The calculated relative cohesive energies of the simple cubic nanoparticles in the size $n = 2000$ and $n = 7000$ are 0.85 and 0.88, respectively, while those of the body-centered nanoparticles in the same size are 0.84 and 0.87, and these of the face-centered nanoparticles in the same size are 0.83 and 0.86. Apparently, if we ignore the structure difference between SC, FCC and BCC structures, more errors may occur in the final results. Furthermore, it is shown that the size effect on the cohesive energy is more obvious in face-centered cubic nanoparticles than that of in the body-centered cubic and the simple cubic nanoparticles. For Mo and W nanoparticles, their cohesive energies calculated by FCC structure are more close to the experimental values than that by SC structure, which also suggests that the present method is efficient in predicting the cohesive energy of nanoparticles by considering the structure difference.

It is known that the melting point of nanoparticle is size dependent [2,3], and melting point is a parameter to estimate strength of the metallic bonds. With the decrease in the particle size, its melting point decreases too, which means that the strength of metallic bond of nanoparticles is weaker than that of bulk metals. The cohesive energy can also be a parameter to characterize the strength of metallic bonds, and the absolute value of cohesive energy of metallic nanoparticle decreases with decreasing of particle size, which also suggests that the metallic bond of nanoparticles is weaker than that of the corresponding bulk metals. Apparently, our theoretical results of metallic bond variation of metallic nanoparticles are consistent with the predictions of that of their melting point variation.

Generally, the differences between the cohesive energies of bulk metals at 0 K and at their melting temperatures are less than 5% [10], while the measuring temperature of the cohesive energy is higher than 0 K but lower than their melting temperature. However, the measuring errors in the values of the cohesive energy of metals are comparable with the temperature effect on the cohesive energy. Therefore, the temperature effect on the cohesive energy of bulk metals can be neglected in citing the experimental values of cohesive energy. According to Eq. (8), the parameters P_0, A_6 and A_{12} are only related to the type of structures and independent of the temperature variation, then the cohesive energy of nanoparticles should follow the same temperature-dependent relation as the bulk metals. In other words, the temperature effect on the cohesive energy of metallic nanoparticles can also be neglected, which has been done in present consideration.

In conclusion, the Lennard–Jones potential is used in this letter to account for the size dependence of the cohesive energy of metallic nanoparticles with different structures by considering the size-dependent potential parameters. It is predicted that the cohesive energy of nanoparticles decreases with the decrease in particle size. The present calculation results on the cohesive energy of Mo and W nanoparticle are reasonably consistent with the corresponding experimental values, which suggests that the simple Lennard–Jones potential can be used to study the properties of nanoparticle by considering the size-dependent potential parameters.

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