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# Generalized bond-energy model for cohesive energy of small metallic particles

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## Abstract

A generalized bond-energy model has been developed to calculate the cohesive energy of nanoparticles by considering the different contributions of face-, edge- and corner-atoms. The model is adapted for metallic particles in a large size range from several atoms to infinity, studying their morphology, phase stability and melting point, etc.

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The cohesive energy of solids is an important property, which can be used to predict other physical properties, such as melting point (MP), the phase stability, etc. It is well known that the cohesive energy of the bulk is constant in specified temperature and pressure [1,2]. For nanoparticles, however, the cohesive energy is size dependent. Unlike the bulk solid, the cohesive energy of nanoparticles is difficult to measure experimentally. Kim et al. firstly reported the experimental cohesive energies of Mo and W nanoparticles until 2002 [3]. They found that the cohesive energy of the nanoparticles is fairly lower than that of the bulk materials. Different models developed to account for the size dependence of cohesive energy, such as BOLS model [4], Latent heat model [5], Liquid drop model [6], surface-area-difference (SAD) model [7] and bond energy (BE) model [8]. The BE model was developed by our group, for explaining the size dependent cohesive energy of Mo and W nanoparticles. Furthermore, the BE model has also been used to predict the melting temperature of nanomaterials [9].

Recently, Prof. Nanda et al. [10] and Dr. Theil have pointed out that the BE model cannot be used to nanoparticles in small size. It is, therefore, needed to generalize the BE model in all size range. It is just the aim of this Letter. Furthermore, a generalized bond energy (GBE) model will also be used to predict the phase stability of nanoparticles in different size and shape.

In the BE model, atoms of a nanoparticle are classified as interior and exterior atoms. The cohesive energy of the nanoparticle is the contributions of both interior and exterior atoms. It is emphasized that the interior atoms are the same as these of bulk materials, and the exterior atoms have large dangling bonds. Then the cohesive energy variation is mainly from the exterior atoms, therefore, rigorous calculation of exterior contributions to cohesive energy determines the limitation of BE model, which is also a key issue in BE model.

The nanoparticles are generally in polyhedral shapes [11–13], in which the exterior atoms are consisted of face-, edge- and corner-atoms, as shown in Fig. 1. In large size particle, the contributions of both edge- and corner-atoms are fairly small compared with the face-atoms. Therefore, it is reasonable to assume all exterior atoms are the face-atoms for large size particles. This is the reason why original BE model can only be

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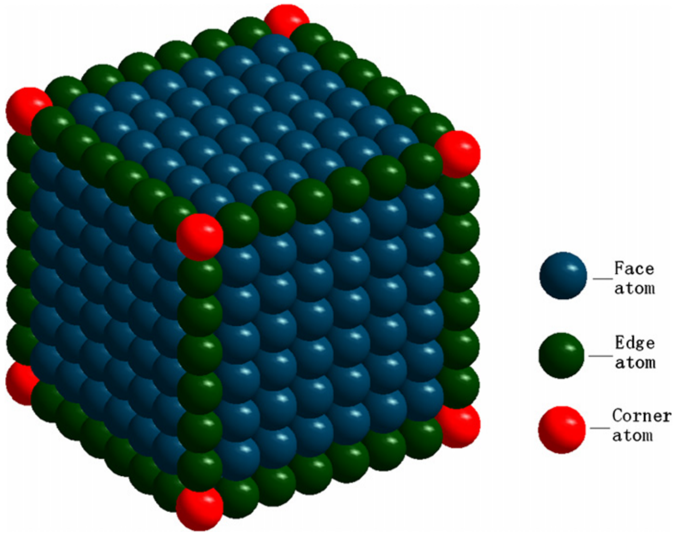

Fig. 1. Different types of exterior atoms in bond energy model.

applied in large particles. Apparently, the original BE model cannot be used to predict the cohesive energy of small particles. Barnard et al. have studied the free energy of polyhedral nanoparticles by considering the contributions given by the corner and the edge atoms [14]. Stimulated by their work, we will also consider the difference between different types of exterior atoms to generalize BE model in this Letter.

For a nanoparticle in polyhedral shape, let $N_i^{\text{face}}$ and $E_i^{\text{face}}$ denote number of face-atoms and cohesive energy per face-atom in the $i$th face, respectively. Similarly, $N_j^{\text{edge}}$ and $E_j^{\text{edge}}$ are the number of edge-atoms and the cohesive energy per atom on the $j$th edge. $E_k^{\text{corn}}$ is the cohesive energy of the corner-atom $k$. Then, the total number of exterior atoms ($N$) can be summed as

$$N=\sum_i N_i^{\text{face}}+\sum_j N_j^{\text{edge}}+\sum_k 1. \tag{1}$$

If $E_0$ denotes the cohesive energy per interior atom, which equals to that of the corresponding bulk materials. Then the total cohesive energy of the nanoparticle with $n$ atoms can be written as

$$E_n=(n-N)E_0+\sum_i N_i^{\text{face}}E_i^{\text{face}}+\sum_j N_j^{\text{edge}}E_j^{\text{edge}}+\sum_k E_k^{\text{Corn}}. \tag{2}$$

If $S_i$ and $\rho_i^{\text{face}}$ are the area and atomic density of the $i$th face, respectively, a total number of atoms in the $i$th face is then $N_i^{\text{face}}=S_i\cdot\rho_i^{\text{face}}$. Similarly, one finds that $N_j^{\text{edge}}=L_j\cdot\rho_j^{\text{edge}}$, where $L_j$ and $\rho_j^{\text{edge}}$ note the length and the atomic density of the $j$th edge. Without relaxation, the cohesive energy of interior atoms equals the value of the corresponding bulk materials as mentioned. Since there exist large dangling bonds for surface atoms, the corresponding cohesive energies of atoms in face, edge and corner can be written as $E_i^{\text{suf}}=\alpha_i E_0$, $E_j^{\text{edge}}=\beta_j E_0$ and $E_k^{\text{corn}}=\lambda_k E_0$, respectively. Furthermore, let $\alpha_i$ denote the number-of-bonds ratio between the face-atoms and interior atoms, $\beta_j$ is the ratio between edge-atoms and interior atoms, and $\lambda_k$ is the ratio between corner-atoms and interior atoms. Therefore, Eq. (2) can be rewritten as

$$\frac{E}{E_0}=\frac{1}{n}\biggl[n-\sum_i S_i\rho_i^{\text{face}}(1-\alpha_i)+\sum_j L_j\rho_j^{\text{edge}}(1-\beta_j)+\sum_k(1-\lambda_k)\biggr]. \tag{3}$$

Eq. (3) can be regarded as the more general formula of BE model. Since the edge atoms and the corner atoms are considered, Eq. (3) can be used to predict the cohesive energy of nanoparticles with different polyhedral morphologies. As a simple case, the Au nanoparticles with different shapes, such as cube, octahedron, cuboctahedron, truncated octahedron and sphere (as shown in Fig. 2), will be discussed. The cube is surrounded by {100} surfaces, and octahedron by {111} surfaces. The surfaces of cuboctahedron and truncated octahedron are surrounded by {100} and {111}. We do not specify the surface of spherical particles, where their surface quantities are regarded as the mean values of {100} and {111}.

To calculate the cohesive energy by using Eq. (3), Au nanoparticle with mentioned shapes is considered firstly. It is assumed that the Au nanoparticle is in ideal Face-Centered-Cubic (FCC) without surface relaxation and reconstruction. If the atomic radius of Au is $r_0$, the atomic face densities ($\rho_i^{\text{face}}$) of {100} and {111} are $1/(4r_0^2)$ and $\sqrt{3}/(6r_0^2)$, respectively. Since the indexes of the edges in Fig. 1(a)–(d) are $\langle 100\rangle$ and $\langle 110\rangle$, the corresponding atomic edge densities ($\rho_j^{\text{edge}}$) are $\sqrt{2}/(4r_0)$ and $1/(2r_0)$, respectively. Both the face densities and the edge densities are easily obtained from the basic cells of FCC structure.

According to simple free electron theory of solids, all positive ions immerged in the electron cloud. In the BE model, the bonds of an atom is assumed to uniformly distribute in the atom surface, therefore, the number of bonds is positively proportional to the atomic surface area immerged in the solids. In GBE model, the interior atoms in nanoparticles are the same as these in the corresponding bulk solids. For face-, edge- and corner-atoms, the number of bonds is related to the parameters $\alpha_i$, $\beta_i$ and $\lambda_k$, respectively. In fact, the parameters $\alpha_i$, $\beta_i$ and $\lambda_k$ can be expressed in one equation, i.e., $=A_{in}/(4\pi r_0^2)$, where $A_{in}$ denotes total surface area per atom. For a face-atom, half its surface is in the solid, thus $\alpha_i=1/2$; the surface of an edge atom is positive proportional to the dihedral angel ($\theta$), thus $\beta_i=\theta/(2\pi)$; similarly $\lambda_k=A_{in}/(4\pi r_0^2)$. The parameters of the Au nanoparticles are listed in Table 1.

The calculated cohesive energies of the Au nanoparticles are shown in Fig. 3, from which following information is found. (1) The cohesive energies of the Au nanoparticles depend on particle size, where the absolute values of cohesive energy increase with increasing the particle size and approach to bulk value; (2) The particle shape affects the cohesive energy, which means that the cohesive energies are different for different shapes even in the identical particle size (the total number of atoms); (3) Among the five shapes studied, the val-

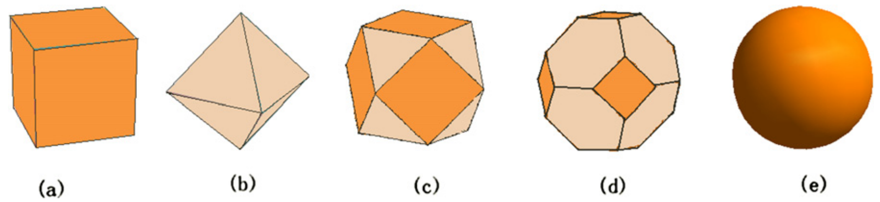

Fig. 2. Au nanoparticles with different shapes: (a) cube; (b) octahedron; (c) cuboctahedron; (d) truncated octahedron; (e) sphere.

Table 1
Input parameters of GBE model for Au nanoparticles

| | Cube | Octahedron | Cuboctahedron | Truncated octahedron | Sphere |
|---|---|---|---|---|---|
| $\alpha_i$ | 0.5 | 0.5 | 0.5 | 0.5 | $0.5(1-0.452/n^{1/3})$[e] |
| $\beta_i$ | 0.250 | 0.281 | 0.348 | 0.281[a], 0.348[b] | |
| $\lambda_k$ | 0.125 | 0.108 | 0.196 | 0.250 | |
| $\rho_i^{\text{face}}$ | $1/(4r_0^2)$ | $\sqrt{3}/(6r_0^2)$ | $1/(4r_0^2)$[c], $\sqrt{3}/(6r_0^2)$[d] | $1/(4r_0^2)$[c], $\sqrt{3}/(6r_0^2)$[d] | $\frac{1/(4r_0^2)+\sqrt{3}/(6r_0^2)}{2}$ |
| $\rho_j^{\text{edge}}$ | $\sqrt{2}/(4r_0)$ | $1/(2r_0)$ | $1/(2r_0)$ | $1/(2r_0)$ | |
| Number of faces | 6 | 8 | 6[c], 8[d] | 6[c], 8[d] | |
| Number of edges | 12 | 12 | 24 | 12[a], 24[b] | |
| Number of corners | 8 | 6 | 12 | 24 | |

[a] Edges between {111} and {111}. [b] Edges between {111} and {100}. [c] Values of {100}. [d] Values of {111}. [e] Considering the curvature of the sphere.

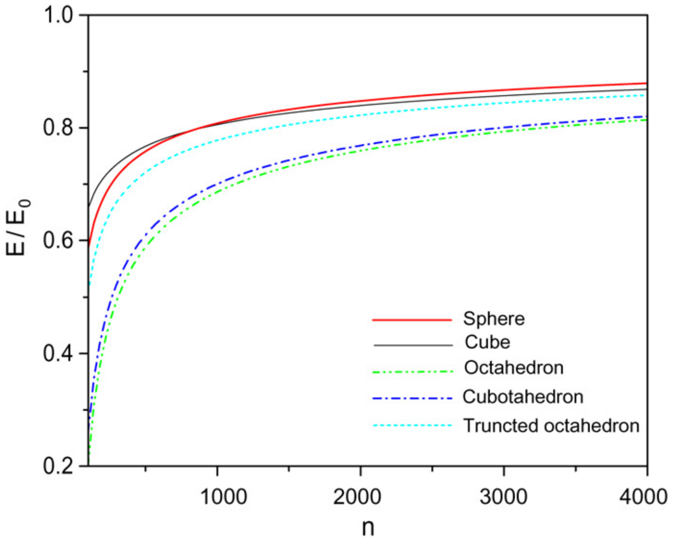

Fig. 3. Cohesive energy of Au nanoparticles with different shapes as the function of particle size.

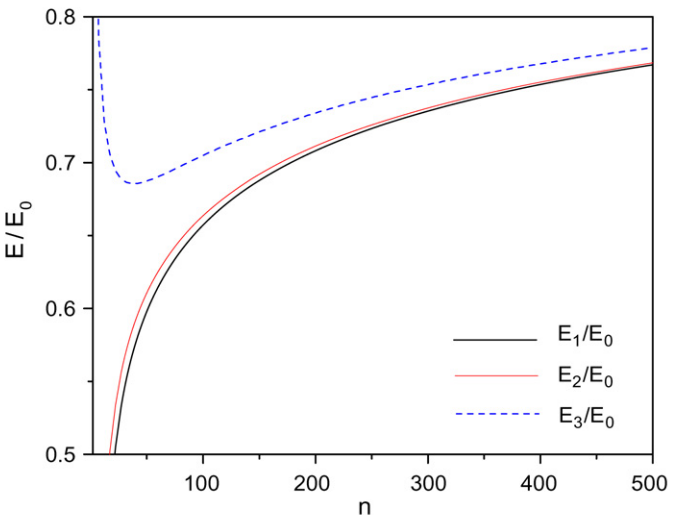

Fig. 4. Cohesive energy of cubic Au nanoparticles as the function of particle size in three cases. $E_1$ denotes the values considering different contributions of face-, edge- and corner-atoms; $E_2$ denotes the values considering of face- and edge-atoms; and $E_3$ denotes the values only considering face-atoms.

ues of the relative cohesive energies follow $E_{\text{Cubic}} > E_{\text{Sphere}} > E_{\text{truncated octahedron}} > E_{\text{cuboctahedron}} > E_{\text{octahedron}}$ when $n < 840$, and $E_{\text{Sphere}} > E_{\text{Cubic}} > E_{\text{truncated octahedron}} > E_{\text{cuboctahedron}} > E_{\text{octahedron}}$ when $n > 840$. In other words, if the nanoparticles keep FCC structure without considering the structure relaxation, they may prefer to cubic shape when $n < 840$ and to spherical shape when $n > 840$.

In the GBE model, the exterior atoms have been grouped as face-, edge- and corner-atoms. For a specified shape, the face- and the edge-atoms increase with increasing the total atomic number ($n$), however, the corner atoms are fixed. For instance, the number of corner atoms of a cubic nanoparticle is 4, which is independent of $n$. To discuss the effects of corner- and edge-atoms on the cohesive energy, three cases have been computed, i.e., (1) considering different contributions of face-, edge- and corner-atoms ($E_1$); (2) only considering the face- and the edge-atoms ($E_2$); (3) only considering the face-atoms ($E_3$). The results are plotted in Fig. 4. It is found that the values $E_2$ are very close to $E_1$, which suggests that the corner-atoms have a little effect on finial results. However, $E_3$ is apparently different from $E_1$ and $E_2$, and the difference between $E_3$ and $E_1$ decreases with increasing particle size. It should be pointed out that the values of $E_3$ are calculated only considering the contribution of face-atoms, which is just the results of original BE model. In Fig. 4, it is also found that the $E_3$ increases when $n < 40$, which is not true. In other words, $n > 40$ can be regarded as the size range of BE model. For GBE model, the

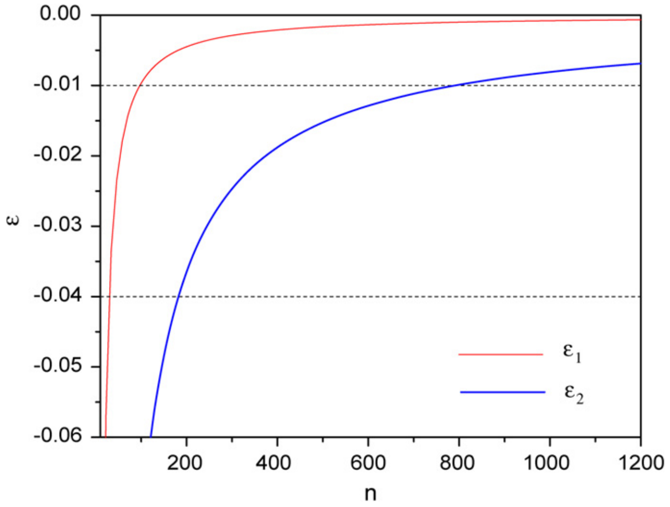

Fig. 5. Critical sizes for ignoring the different contributions of corner-atoms (or both edge- and corner-atoms) when calculation of the cohesive energy of nanoparticles.

range is enlarged. For cubic Au nanoparticles, the size range of GBE model is $n > 6$. Although the quantum effect should also be considered when the number of atoms approaches to one decade, the present generalization broaden the application scope of BE model.

According to GBE model, all face-, edge- and corner-atoms should be considered. However, in some cases, the contributions of the edge- and the corner-atoms can be ignored. For instance, all the atoms vibrate in the equilibrium positions at non-zero absolute temperature, thus the cohesive energies also change a little around a constant. If the energy variation resulting from the lattice vibration is larger than the contributions from the edge and the corner atoms, the latter contributions can reasonable be ignored. To study what sizes are the critical sizes for ignoring the edge- and the corner-atoms, we introduce two parameter $\varepsilon_1$ and $\varepsilon_2$, where the $\varepsilon_1$ and $\varepsilon_2$ are defined as $\varepsilon_1 = (E - E')/E$, $\varepsilon_2 = (E - E'')/E$, respectively. Here $E$ denotes the cohesive energy by considering of the different contributions of face-, edge- and corner-atoms, $E'$ denotes the cohesive energy by ignoring the corner-atoms, and $E''$ ignoring both edge- and corner-atoms.

If the error from lattice vibration (or other reasons) is $\varepsilon_0$, we can give two critical sizes $n_1$ and $n_2$ by comparing $\varepsilon_0$ with $\varepsilon_1$ and $\varepsilon_0$ with $\varepsilon_2$, where $n_1$ is the size of ignoring the corner-atoms and $n_2$ is the size of ignoring both edge- and corner-atoms. In other words, if $n > n_1$, the corner-atoms can be ignored; if $n > n_2$, both edge- and the corner-atoms can be ignored. Apparently, we have $n_2 > n_1$. As an example, we calculate the critical sizes of Au nanoparticles with cubic shape, and the calculated results are shown in Fig. 5. If $\varepsilon_0 = 0.01$, then $n_1 = 29$ and $n_2 = 180$; if $\varepsilon_0 = 0.04$, then $n_1 = 97$ and $n_2 = 790$. These values depend on the error $\varepsilon_0$, which suggests that we can determine whether to consider the edge- and the corner-atoms according to real cases studied.

To test the efficiency of GBE model, we should compare our calculated results with experimental values. Kim et al. reported the experimental values of the cohesive energies of Mo and W nanoparticles as mentioned [3], and the calculated values given by BE model are consistent with these results except for $n = 30$ [8]. As mentioned, the BE model is valid for $n > 40$, and the GBE is valid for $n > 6$, which suggests that GBE model may be used to calculate the cohesive energy of W nanoparticles with $n = 30$ (W-30). Based on the calculation results discussed, we assume that the W-30 particle is in cubic-like shape. As Kim et al. mentioned, the W-30 particle is in amorphous structure. For amorphous structure, if the interactions between the nearest atoms are only considered, its coordination number is similar to that of FCC structure. We used Eq. (3) to perform our calculation, where the parameters adopted the values in Table 1 (the atomic radius denotes the value of W). The calculated cohesive energy of W-30 particle by GBE model is 449 kJ/mol, which is close to the experimental value 590 kJ/mol [3]. The difference may be caused by the following reason: (1) the relaxation is not considered; (2) the shape may not be the ideal cubic. All in all, the result is acceptable for a thermodynamic model. This example also shows that the GBE model can be applied to small particles.

It should be mentioned that the GBE model can deal with not only face-centered-cubic structure, but also other structures. To calculate the cohesive energy of other structures, the model parameters should be modified according to the structure properties. Another, the GBE is a more general model for the cohesive energy of nanoparticles, where the BE model can be regarded as an approximation of GBE model. Furthermore, the present GBE model is based on ideal structures, thus the structure relaxation is not considered. The structure relaxation can be regarded as a spontaneous process at the constraints of thermodynamic laws. After relaxation, the free energy of the system will decrease, and the structure will be more stable. Therefore, the relaxed cohesive energy will be higher than the un-relaxed one (given by GBE model).

In conclusion, the BE model is generalized by considering the contributions to cohesive energy of face-, edge- and corner-atoms. The model can be used to study the surface morphology, the phase stability, etc., of nanoparticles. By calculation the cohesive energies of Au nanoparticles in cubic, spherical, octahedral, cuboctahedral and truncated octahedral shapes, it is found that the Au nanoparticle may prefer to spherical shape when $n > 840$, and prefer to cubic when $n < 840$. Furthermore, the calculated cohesive energy of W particles with 30 atoms by GBE model is 449 kJ/mol, which is close to experimental value 590 kJ/mol.

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