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Generalized Surface-Area-Difference model for cohesive energy of nanoparticles with different compositions

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Abstract The Surface-Area-Difference (SAD) model has been generalized to account for the cohesive energy of nanoparticles with different compositions (NDC) in different shape, where the particle shape is described by the shape factor. It is found that the cohesive energy of NDC depends on the particle size, the particle shape and the atomic percent of each composition, which can be simply regarded as mathematical mean values of the cohesive energies of all the compositions.

The cohesive energy of nanoparticles depends on the particle size, which has been confirmed by recent experiments [1] and explained by different models [2–7]. The first experimental values of the cohesive energy of pure Mo and W nanoparticles have been reported in 2002 [1], where the cohesive energy is determined by measuring the oxidation enthalpy of the corresponding oxidations of nanocrystals. Some researchers have developed different models to explain the size dependent cohesive energy [2–7]. One of these models is called as Surface-Area-Difference (SAD) model [3, 4], which is based on the basic concept of cohesive energy. The SAD model is developed by our group, which has been introduced in a review article by professor Sun [8]. However, the published SAD model can only account for the cohesive energy of pure metallic nanoparticles, but not for that of nanoparticles with different compositions (NDC). In this letter, we will generalize SAD model to account for the cohesive energy of NDC.

Since the cohesive energy of a material is the energy to divide the material into isolated atoms, in other words, the direct result of cohesive energy is to create new surface. The increased surface energy should equal the cohesive energy of the material, which results from the surface area difference between the total isolated atoms and the material. This is the basic concept of SAD model [3, 4]. In SAD model, the surface of the material approximately denotes the first layer of the material. In the following, we will give the generalized SAD model.

We assume that a nanoparticle consists of m compositions, i.e., $A_i (i = 1, 2, \cdots m)$, where A_i denotes the composition i. The atomic percent of each element A_i is $x_i (i = 1, 2, \cdots m)$, where $\sum_{i=1}^{m} x_i = 1$. The total number of atoms is n, and the number of atoms of A_i is $x_i n$. The atomic diameter of A_i is denoted as d_i, and the surface energies per unit area of A_i is γ_i. The surface energy of A_i with nx_i atoms is $nx_i \pi d_i^2 \gamma_i$, and then the total surface energy of n atoms is $\sum_{i=1}^{m} nx_i \pi d_i^2 \gamma_i$.

If the surface of the NDC is spherical, its surface energy is $4\pi D^2 \gamma$, where D is the diameter of the nanoparticle and γ is the surface energy per unit area. Without considering the surface segregation, the surface energy per unit area can be estimated by the following equation, i.e.

$$\gamma = \sum_{i=1}^{m} x \gamma_i \tag{1}$$

For a non-spherical nanoparticles, the surface energy can be written as $\pi \alpha D^2 \gamma_i$, where α is shape factor. Shape factor is defined as the surface area ratio of non-spherical

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nanoparticle and spherical nanoparticle in identical volumes. For spherical nanoparticles, we have $\alpha = 1$, and for non-spherical nanoparticle, $\alpha > 1$ (For instance, the shape factor of cubic nanoparticles equals 1.24). The details of shape factor have been presented in reference [9, 10].

Since the NDC consists of n atoms, the volume of NDC equals the volumes of n atoms, i.e., $f \cdot \pi D^3/6 = \sum_{i=1}^{m} n x_i \pi d_i^3/6$, where f is the packing factor (e.g., f=0.74 for face-centered-cubic structure). Then we have

$$n = \frac{f \cdot D^3}{\sum_{i=1}^{m} x_i d_i^3} \tag{2}$$

According to SAD model, the surface energy difference between the nanoparticle and its total atoms is the cohesive energy of nanoparticle. Therefore, the cohesive energy of NDC (E_n) can be written as

$$E_n = \sum_{i=1}^{m} \left(n x_i \pi d_i^2 \gamma_i \right) - \pi \alpha D^2 \gamma. \tag{3}$$

By considering Eq. (1), the cohesive energy per mole (E_c) of the NDC can be written as

$$E_c = N_0 \sum_{i=1}^{m} x_i \pi d_i^2 \gamma_i \left(1 - \frac{\alpha D^2}{n d_i^2} \right), \tag{4}$$

where N_0 is the Avogadro's number.

According to SAD model, the mole cohesive energy of the corresponding bulk A_i is $E_i = N_0 \pi d_i^2 \gamma_i$ [3], and then we can rewrite Eq. (4) as

$$E_c = \sum_{i=1}^{m} x_i E_i \left(1 - \frac{\alpha D^2}{n d_i^2} \right). \tag{5}$$

In our previous work, the pure metallic nanoparticle is only discussed [3], which is a special case of Eq. (5). For instance, for pure spherical nanoparticles, we have m=1, x_1 =1 and α =1. Equation (2) is reduced to $n = D^3/d_1^3$, and Eq. (5) is simplified as $E_c = E_1 (1 - d_1/D)$, which is just the expression obtained in our previous work. Apparently, Eq. (5) is the more general relation of SAD model, which shows that the cohesive energy of NDC not only depends on the atomic percent, the diameter and the cohesive energy of each component, but also depends on the size and the shape of NDC.

Here we take $Cu_x Au_{1-x}$ nanoparticles for example. The atomic percent of Cu ranges from 0 to 1. For regular polyhedral shape, the shape factor is larger than 1 (spherical) but smaller than 1.49 (regular tetrahedral) [9], and then the two values 1 and 1.49 have been chosen in our calculation. The atomic diameters of Cu and Au are 0.2556 nm and 0.2884 nm [11], and their cohesive energies are 336 kJ/mol and 368 kJ/mol [12], respectively. The calculation results are shown in Figs. 1–3. It is shown that the cohesive energy of Cu–Au nanoparticles decreases with decreasing the particle size in a specific shape, and the variation tendency is the same as that of pure metallic nanoparticles. Furthermore, the cohesive energy of Cu–Au nanoparticles also depends on the atomic percent of each composition. For $Cu_{0.703} Au_{0.297}$ nanoparticles (Fig. 3), the cohesive energy given by semi-empirical model [13] lies in the middle of the present calculated curves α =1 and α =1.49, which suggests that the $Cu_{0.703} Au_{0.297}$ nanoparticles may be in polyhedral shape. The present theoretical results are also close to these calculated by many-body potential [14]. According to the present model, the cohesive energy of NDC can be simply regarded as mathematical mean values of the cohesive energies of all the compositions (Eq. (6)).

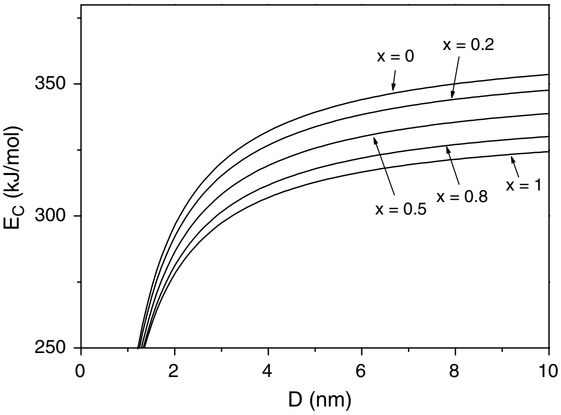

Fig. 1 Cohesive energy of $Cu_x Au_{1-x}$ nanoparticles as the function of particle size. The solid lines are calculated from Eq. (5), where the shape factor equals 1

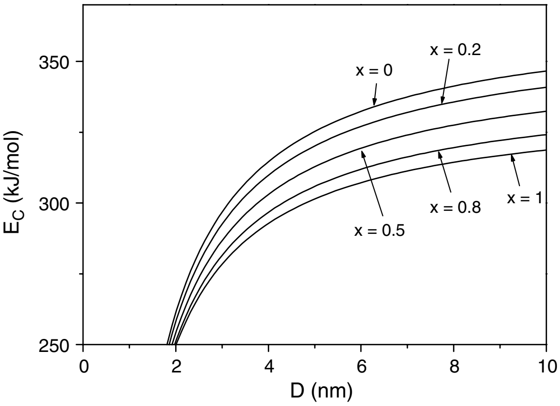

Fig. 2 Cohesive energy of $Cu_x Au_{1-x}$ nanoparticles as the function of particle size. The solid lines are calculated from Eq. (5), where the shape factor equals 1.49

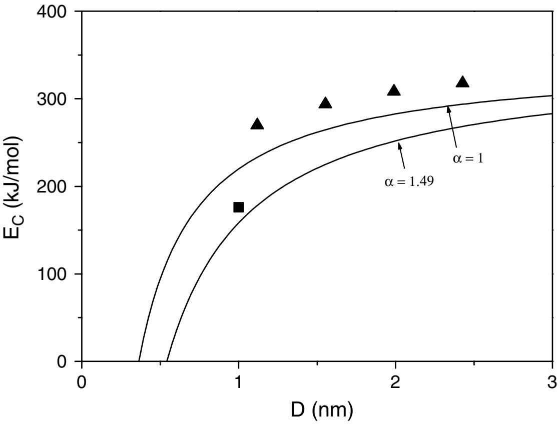

Fig. 3 Cohesive energy of $Cu_{0.703}$ $Au_{0.297}$ nanoparticles as the function of particle size. The solid lines are calculated from Eq. (5), where the shape factor equals 1 and 1.49. The symbol ''■'' denotes the result of semi-empirical model [13], and the symbols ''▲'' denote the values calculated by many body potential [14]

In conclusion, we have generalized SAD model to account for the cohesive energy of NDC. It is shown that the cohesive energy of NDC depends on the particle size, the particle shape and the atomic percent of each composition. Since cohesive energy is a very important thermodynamic quantity of materials (many thermodynamic quantities can be calculated by the cohesive energy), the generalized SAD model can be used to predict the thermodynamic properties of NDC in designing new nanomaterials.

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