

A simplified model to calculate the higher surface energy of free-standing nanocrystals

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A simple but valid equation for the higher surface energies of metallic nanocrystals is obtained. The calculated values on

surface energies of Ag and Au nanocrystals are in excellent agreement with the corresponding newest experimental values.

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The special properties of nanocrystals have generated great interest in both scientific and technological communities, and the investigations on size dependent thermodynamic parameters have been topics of interest in recent years. Despite significant progress in studies of thermodynamic properties of nanocrystals, some important problems have not received unambiguous solutions. One of the most interesting and important questions relates to the surface energy of nanocrystals. It is indeed surprising that this fundamental problem is still under debate, for there exist three opposite viewpoints on the solid–vapor surface energy of metallic nanocrystals. Take three outstanding groups which focus on the mentioned topic for example: Alymov and Shorshorov came to the conclusion that the value of surface energy of metallic nanocrystals is size and structure independent and equal to the corresponding bulk value by theoretically extending the thermodynamic potential function of small particle got from the same research group [1]; Lu and Jiang established a model for size dependent surface energy of nanocrystals based on their previous model for the size dependent cohesive energy, and found that the surface energy falls as the size of crystals decreases to several nanometers [2–4]; while Nanda et al. experimentally determined the size independent surface energies of free fcc Ag and Au nanoparticles by presenting accurate online heat treatment for the study of size dependent evaporation of nanoparticles relating to the Kelvin effect, and they found the values of surface energies measured to be significantly higher as compared to that of the bulk [5, 6]. Furthermore, the latter two groups made an interesting de-

bate by releasing a series of high quality literature [4–6] in the latest two years that raised the attractiveness of this topic.

In this short letter, a simple but valid equation for higher surface energies of metallic nanocrystals is obtained, and the calculated values on surface energies of Ag and Au nanocrystals are in excellent agreement with the corresponding newest experimental values measured by Nanda et al. [5, 6].

Considering that the stability of superficial atoms and interior atoms of crystals is quite different, the total cohesive energy can be written as the sum of the total interior part and the total superficial part [7–10]. It is known that the cohesive energy equals the energy that can divide the nanocrystal into isolated atoms by destroying all bonds, that is to say, the cohesive energy is directly decided by the product of the number of bonds and the bond energy [7–10]. Based on the concept of the cohesive energy mentioned above, then a simplified equation on cohesive energy is obtained [8]

$$E_n = (1 - \alpha) E_b + \alpha E_s, \quad (1)$$

where E denotes cohesive energy, the subscripts n, b and s denote nanoparticle, bulk and surface, respectively, α denotes the surface-to-volume atomic ratio. Suppose the number of bonds of interior atom is m , considering the surface relaxation, only about one-fourth of the area of each surface atom will be embedded in the lattice [11], which means the number of the bonds of a surface atom with inte-

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rior atoms is $(1/4)m$ for simplicity [7, 8, 11]. Then Eq. (1) can be rewritten as [8]

$$E_n = E_b \left(1 - \frac{3}{4} \alpha\right). \quad (2)$$

Suppose the shape of the nanoparticle is ideal cubic, we have

$$E_n = E_b \left(1 - \frac{6}{n^{1/3} C^{2/3} \pi k^2}\right), \quad (3)$$

where n denotes the atomic number of the nanocrystal, C is the atomic number of one structure cell, and k is the ratio between equivalent atomic radius and lattice parameter. For fcc, bcc and hcp structures, C are 4, 2 and 2, and k are $\sqrt{2}/4$, $\sqrt{3}/4$ and $1/2$, respectively [12].

In order to describe the difference between non-cubic and cubic particles, we have defined [8, 13] the shape factor μ being the ratio of two surface areas

$$\mu = S'/S, \quad (4)$$

where S' is the surface area of a particle in any shape, and S is the surface area of a cubic particle which has the same volume as the particle with previous shape. Then the cohesive energy of a nanoparticle with random shape can be described as

$$E_n = E_b \left(1 - \frac{6\mu}{n^{1/3} C^{2/3} \pi k^2}\right). \quad (5)$$

On the other hand, let us come to another important thermodynamic parameter of nanoparticles – the surface energy. It is helpful to imagine that the process of forming a fresh surface of a nanoparticle is divided into two steps: firstly, the nanoparticle is cleaved from the corresponding bulk so as to expose the new surface, keeping the atoms fixed in the same positions that they occupied when in the bulk phase; and secondly, the atoms in the surface region are allowed to rearrange to their final equilibrium positions, by spontaneously reducing the cohesive energy and enhancing the surface energy. In the case of liquid, these two steps occur as one, but with solids the second step may occur only slowly because of the immobility of the surface region [11]. Thus, with a solid it may be possible to stretch or to compress the surface region without changing the number of surface atoms in it. From the energy point of view, according to the discussions mentioned above, we can write the following expression on cohesive energy and surface energy of a nanoparticle for simplicity:

$$nE_b - nE_n = S\gamma_n \Rightarrow E_n = E_b - \frac{6\mu a^2 \gamma_n}{n^{1/3} C^{2/3}}, \quad (6)$$

where γ_n denotes the surface energy of the nanoparticle, S the surface area, and a is the lattice parameter. It is noteworthy that the form of Eq. (6) is very similar to the classical model on atomic clusters [14–16], although the physical origins of both models are different.

Table 1 Calculated surface energies and the input constants of fcc Ag and Au nanocrystals. Note that the E_b value in eV should be transformed to J/m² by 1 eV = 1.6×10^{-19} J.

	E_b (eV) [18]	K [12]	a (Å) [18]	γ_n (J/m ²) (Cal.)	γ_n (J/m ²) (Exp.)
Ag	2.95	$\sqrt{2}/4$	4.09	7.2	7.2 [5]
Au	3.81	$\sqrt{2}/4$	4.08	9.3	9.0 [6]

By combining Eq. (3) and Eq. (6), a simplified formula for the surface energy of a nanocrystal can be given:

$$\gamma_n = \frac{E_b}{\pi k^2 a^2}. \quad (7)$$

From Eq. (7) we can see that the surface energy of the nanocrystal is size independent, which implies that the constant of surface energy is an intrinsic property of the nanocrystal compared with its bulk value.

In order to confirm the validity of Eq. (7), the γ_n values of free fcc Ag and Au nanoparticles are calculated and listed in Table 1, and the results 7.2 J/m² for Ag nanoparticles and 9.3 J/m² for Au nanoparticles are quite in agreement with the experimental values 7.2 J/m² for Ag [5] and 9.0 J/m² for Au [6] respectively, which are apparently significantly higher than the corresponding bulk values of 1.25 J/m² and 1.5 J/m² [17], respectively.

Since most thermodynamic parameters such as cohesive energy, melting temperature, melting entropy, melting enthalpy and vacancy formation energy etc. are reported size dependent and proportional to the reciprocal of size, it is hard to make such a conclusion that the surface energy of nanoparticles is size independent and much higher than that of corresponding bulk. However, the indirect implication of higher values of the surface energy reported from other discussions [19–21], and especially the newest experimental results [5, 6], support the above-mentioned conclusion.

Despite the success of our calculations in this letter, several questions should be further discussed in future: (1) how to find out the critical size of the mutation of surface energy theoretically; (2) how to get a more comprehensive and more precise expression on the surface energy by considering different facets and different types of bonds of nanoparticles.

In summary, a simple but valid equation for the higher surface energies of nanocrystals is obtained, the calculated results of Ag and Au nanocrystals are in excellent agreement with corresponding experimental values, which are apparently significantly higher than the corresponding bulk values.

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