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LETTER TO THE EDITOR

A simplified model to calculate the surface-to-volume atomic ratio dependent cohesive energy of nanocrystals

D Xie, M P Wang and W H Qi

School of Materials Science and Engineering, Central South University, Changsha, 410083, People's Republic of China

E-mail: xiedan_cat@sina.com

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Abstract

A simplified model for the surface-to-volume atomic ratio dependent cohesive energy of nanocrystals is obtained in this letter. On the basis of the model, we predict that the cohesive energy can not only decrease but also increase with the increasing surface-to-volume atomic ratio under different conditions. The model predictions are found to be in agreement with the experimental values of Mo and W nanoparticles. The conditions on the cohesive energy of an embedded nanocrystal increasing or decreasing with the increasing surface-to-volume atomic ratio are discussed. The relations between the cohesive energy of nanoparticles, nanowires and nanofilms, and the shape effect on nanoparticles are also discussed. Since the cohesive energy is regarded as being directly related to the nature of the thermal stability of nanocrystals, the relationship to the phenomenon of melting and superheating given by our cohesive energy model seems sensible.

The special properties of nanocrystals have generated great interest in both scientific and technological communities, and the phenomenon that nanocrystals size-dependent cohesive energy occurs has been a topic of interest in recent years. The cohesive energy of nanocrystals, which can be determined by experiment [1] and computed by different theoretical models such as the SE model [2], the BE model [3], the Lennard-Jones potential model [4], Jiang's model [5], the liquid-drop model [6–8], the bond-OLS model [9, 10], etc, is regarded as directly related to the nature of the thermal stability of nanocrystals [1]. Most of the theoretical calculations of cohesive energy are inconvenient because several parameters which are not easy to estimate by experiments are required as input, and few of them can predict that cohesive energy can increase in some conditions such as the liquid-drop model [6–8]. But unfortunately, the liquid-drop model cannot predict the cohesive energy accurately enough, which we will discuss later.

In this letter, a simplified but accurate and comprehensive model, which can not only describe the decrease but also the increase, is developed to account for the size effects of nanocrystals.

Considering that the stability of superficial atoms and interior atoms of crystal are quite different, we write the total cohesive energy as the sum of the total interior part and the total superficial part, then a simplified equation for the cohesive energy is obtained

$$nE_c = (n - n_s)E_i + n_sE_s \quad (1)$$

where n denotes the total number of atoms, E denotes the mean cohesive energy per atom and the subscripts c, s, i mean crystal, superficial and interior, respectively. According to the definition of the surface-to-volume atomic ratio α [11], equation (1) can be rewritten as

$$E_c = (1 - \alpha)E_i + \alpha E_s. \quad (2)$$

For bulk materials α approaches 0, then

$$E_b = E_i. \quad (3)$$

According to equations (2) and (3), we have

$$E_n = (1 - \alpha)E_b + \alpha E_s \quad (4)$$

where the subscripts n and b mean nanocrystal and corresponding bulk, respectively. 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 [3]. Based on the concept of the cohesive energy mentioned above, and considering the surface relaxation, for simplicity the mean cohesive energy per surface atom E_s can be described approximately as follows

$$E_s = (1 - \beta)\frac{E_i}{4} + \beta \left\{ \frac{E_i}{4} + \frac{3}{4}[(E_i/2) + k(E_m/2)] \right\}$$

i.e.

$$E_s = (1 - \beta)\frac{E_b}{4} + \beta \left\{ \frac{E_b}{4} + \frac{3}{4}[(E_b/2) + k(E_m/2)] \right\} \quad (5)$$

where β is the ratio of the interface area to the whole surface area, k denotes the degree of coherence between nanocrystal and matrix, and the subscript m means matrix. For a nanocrystal wholly embedded in the matrix, $\beta = 1$, and for a crystal not embedded in any matrix, $\beta = 0$. $k = 1$ means a completely coherent interface between the nanocrystal and matrix, while $k = 0$ means an incoherent interface. According to equations (4) and (5), the surface-to-volume atomic ratio dependent cohesive energy of nanocrystals can be described as

$$E_n = E_b + \frac{3}{8}\alpha[k\beta E_m - (2 - \beta)E_b]. \quad (6)$$

According to equation (6), the cohesive energy of wholly free-standing nanocrystals and wholly embedded nanocrystals are given by

$$E_n = E_b(1 - \frac{3}{4}\alpha) \quad (7)$$

$$E_n = E_b + \frac{3}{8}\alpha(kE_m - E_b). \quad (8)$$

From equation (7) we can see that the cohesive energy of wholly free-standing nanocrystals decreases with their increasing surface-to-volume atomic ratio, and such a conclusion is consistent with the corresponding experiments which the theoretical models qualitatively predict [1–10]. In order to prove the quantitative effectiveness of our method, the cohesive energy of Mo and W metallic nanoparticles are calculated based on equation (7). The results of our equivalent model and the liquid-drop model [6] and experimental values [1] are all shown in figure 1.

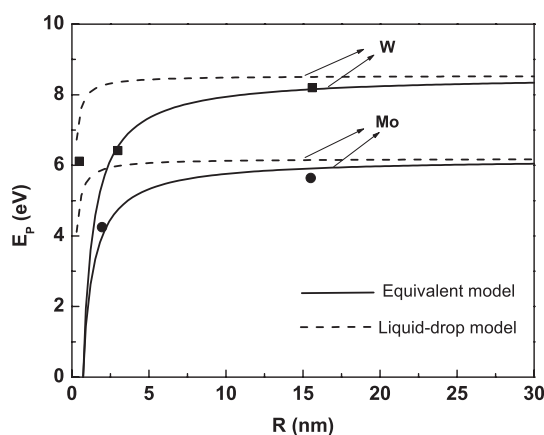


Figure 1. The cohesive energy for Mo and W nanoparticles as a function of particle size R (or the surface-to-volume atomic ratio, $\alpha = 3d/R$ [11], where d denotes the atomic diameter). The solid curves denote the calculations of our equivalent model corresponds to equation (7), the dashed curves denote the calculations of the liquid-drop model. For Mo, $E_b = 6.19$ eV and $d = 0.30988$ nm. For W, $E_b = 8.54$ eV and $d = 0.31170$ nm. The symbols (●) and (■) denote the experimental values of Mo and W nanoparticles, respectively [10].

It is apparent that the predictions of our model are more consistent with the experimental values than the liquid-drop model [1, 6], except for the value of a W nanoparticle of 0.97 nm which results from the fact that our model mainly deals with a crystal lattice structure not an amorphous structure, and our previous work on the discussion of the minimum critical size of a nanocrystal has confirmed that such a W nanoparticle is no longer crystalline [12]. In other words, all equations obtained in this letter are mesoscopic formulae.

From equation (8) we can see that the cohesive energy of wholly embedded nanocrystals decreases or increases with their increasing surface-to-volume atomic ratio, and the decrease or increase depends on two parameters, one is the cohesive energy of the bulk matrix E_m , the other is the degree of coherence k between nanocrystal and matrix.

Suppose the interface between nanocrystal and matrix is coherent, the surface-to-volume atomic ratio dependent cohesive energy E_m is shown in figure 2. It is easy to find that the cohesive energy increases when E_m is more than E_b , and decreases when E_m is less than E_b , and the magnitude of the decrease is less than that of a free-standing nanocrystal.

According to equation (8), the condition that cohesive energy increases with their increasing surface-to-volume atomic ratio is

$$E_m > E_b/k. \quad (9)$$

We know that the cohesive energy of a nanocrystal is a parameter used to estimate the strength of bonds, and the melting point can also be a parameter used to characterize the strength of bonds, which means the cohesive energy and melting point may have some proportional relations [9, 12]. Apparently, our theoretical results of cohesive energy variation are consistent with the predictions of that of their melting point variation. It is easy to show that only when equation (9) is satisfied does the cohesive energy increase, or superheating occur, which means that superheating occurs when

$$T_m > T_b/k \quad (10)$$

where T_m denotes the melting point. It is known that if the interface between nanocrystal and matrix is coherent and the melting point of the matrix is higher than that of the nanocrystal,

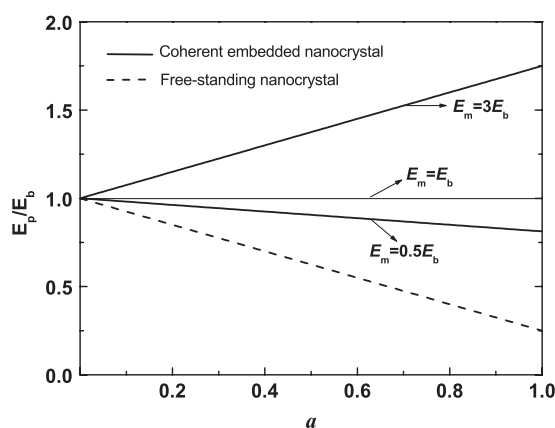


Figure 2. The prediction of the surface-to-volume atomic ratio dependent cohesive energy of nanocrystals embedded in different matrixes with coherent interfaces given by our equivalent model.

superheating occurs [13–16]; such a conclusion is consistent with our theory. Since the experimental values on cohesive energy of embedded nanocrystals have not been obtained at the present time, we cannot prove the quantitative effectiveness of our method directly.

We have calculated that if nanoparticles, nanowires and nanofilms have the same size, the ratio of α is 3:2:1 [11]. According to equation (6), it is easy to get that $E_p > E_w > E_f$, where the subscripts p, w, f denote particle, wire, film, respectively. That is to say, as the dimensions of the nanocrystal increase, the thermal stability decreases. Since the experimental values on cohesive energy of nanowires and nanofilms have not been obtained at the present time, we cannot prove the quantitative effectiveness of our method directly.

In our letter, the effect of temperature on the cohesive energy and the crystal lattice distortion are both ignored due to their smallness. It is reported that the thermodynamics of nanoparticles are size and shape dependent [10, 15, 17–19], and the shape effect is not a small quantity [17–19]. Although most size dependences are calculated for spherical particles, there are some papers which discuss the shape effect of nanoparticles [17–19]. In order to describe the difference between non-spherical and spherical particles, we have defined [11, 12, 20] the shape factor μ as the ratio of two surface areas

$$\mu = S'/S \quad (11)$$

where S' is the surface area of a non-spherical particle, and S is the surface area of a spherical particle which has the same volume with the previous shape. Then the surface-to-volume atomic ratio of nanoparticles is obtained [11]

$$\alpha' = 3\mu d/R. \quad (12)$$

From the discussion above, it seems that the calculation of the cohesive energy of nanoparticles by equation (6) will be more precise if α is used instead of α' .

In conclusion, a simplified model is developed in this letter to account for the surface-to-volume atomic ratio dependence of the cohesive energy of nanocrystals. With increasing surface-to-volume atomic ratio, the cohesive energy can not only decrease but also increase. Furthermore, our predictions on the cohesive energy of Mo and W nanoparticles are consistent with the corresponding experimental values. The condition for the cohesive energy of the embedded nanocrystal to increase or decrease, the relations of the cohesive energy of nanoparticles, nanowires and nanofilms, and the shape effect of nanoparticles are discussed in

our letter. As the cohesive energy is a very important quantity which is related to the nature of the thermal stability of nanocrystals directly, we are confident that the method developed in this letter will play an important role in theory and experiment.

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