Comment on "Size effect on the cohesive energy of nanoparticle"—Extending the model available for embedded nanoparticle

D. XIE*, M. P. WANG, L. F. CAO
School of Materials Science and Engineering, Central South University, Changsha 410083, People's Republic of China
E-mail: xiedan_cat@sina.com

Recently, Qi *et al.* developed a simple continuous medium model to account for the size-dependent cohesive energy of nanoparticle [1]. In spite of the success, the size-dependent cohesive energy of embedded nanoparticle cannot be predicted by the model obtained in that letter. Though the cohesive energy of a free-standing nanoparticle is known to decrease as its size decreases by experiment in recent years [2], nanoparticle embedded in a matrix increase or decrease the cohesive energy of the corresponding bulk cannot be testified by experiment, and only a few of theoretical models begin to focus on explaining such phenomena which directly relate to superheating of nanoparticle in latest 2 years [3, 4]. In this letter, the continuous medium model developed by Qi *et al.* will be extended to make it available for embedded nanoparticle.

According to Qi's consideration, the way to determine the cohesive energy E_P of nanoparticle is to consider the difference between the surface area of a whole particle and the overall surface area of all the constituent atoms in isolated state, then E_P can be regarded as the energy required to generate the area difference (See Equation 5 and 11 of Ref. [1]). The above-mentioned approach can predict free-standing nanoparticle and corresponding bulk well, but when it comes to predicting embedded nanoparticle it should be modified. Let us suppose there exists a bulk matix which has a vacancy that can embed the nanoparticle with perfect coherency, when the nanoparticle is embedded in the vacancy of matrix, both the surface of nanoparticle and vacancy in matrix disappeared with the interface between the nanoparticle and the matrix created, then the decreasing energy caused by the disappearance of surfaces can be regarded as the increasing part of cohesive energy of free-standing nanoparticle. Based on the discussion mentioned above, we have

$$E'_P = E_P + \pi D^2 \cdot \left(\frac{\gamma_0 + \gamma_m}{2}\right) \tag{1}$$

where E'_P denotes the cohesive energy of embedded nanoparticle, the subscript m means matrix.

By inserting Equations 10 and 11 of Ref. [1] in the above equation, we can get

$$E'_P = E_b\left\{1 - \frac{d}{D}\left[\frac{1}{2}\left(1 - \frac{\gamma_m}{\gamma_0}\right)\right]\right\} \tag{2}$$

Then the size-dependent cohesive energy of nanoparticle can be described as follows

$$E_P = \begin{cases} E_b \cdot \left(1 - \dfrac{d}{D}\right) & \text{(free-standing)} \\ E_b \cdot \left\{1 - \dfrac{d}{D}\left[\dfrac{1}{2}\left(1 - \dfrac{\gamma_m}{\gamma_0}\right)\right]\right\} & \text{(embedded)} \end{cases} \tag{3}$$

From Equation 2 we can see that if γ_m is more than γ_0, the cohesive energy of embedded nanoparticle will increase with the decreasing size, and vice versa.

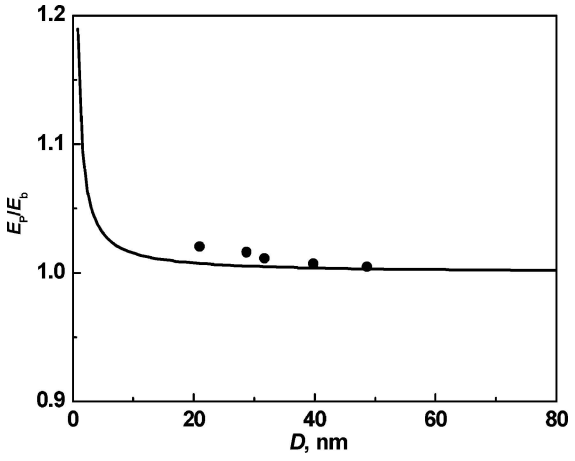

Figure 1 Size-dependent cohesive energy of Ag nanoparticle embedded in Ni matrix. The solid line denotes the caculation results given by Equation 2, and the symbols denote the values converted by experimental values of melting point [8]. Note that the atomic diameter of Ag is 0.3194 nm, the cohesive energy of bulk Ag is 284 kJ/mol [9], the surface energy of Ag and Ni are 1250 mJ/m^2 and 2450 mJ/m^2, respectively [10].

*Author to whom all correspondence should be addressed.

In order to prove the quantitative effectiveness of Equation 2 in this letter, we should compare the prediction results with experimental values. But till now there are not available any experimental values on the cohesive energy of embedded nanoparticle. In other words we know that the cohesive energy of nanocrystal is a parameter used to estimate 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 have some proportional relations [5–7]. Apparently, our theoretical results on cohesive energy variation of embedded nanoparticle will be consistent with the predictions of that of their melting point variation if the model is correct. Here we compare the the cohesive energy variation caculated by the continuous medium model with that converted by experimental values of melting point [8] (see Fig. 1). It is easy to find that our theoretical results are consistent with the values given by the melting point variation, which means Equation 2 obtained in this letter is correct and effective.

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