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Size and shape dependent lattice parameters of metallic nanoparticles

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Abstract

A model is developed to account for the size and shape dependent lattice parameters of metallic nanoparticles, where the particle shape difference is considered by introducing a shape factor. It is predicted that the lattice parameters of nanoparticles in several nanometers decrease with decreasing of the particle size, which is consistent with the corresponding experimental results. Furthermore, it is found that the particle shape can lead to 10% of the total lattice variation. The model is a continuous media model and can deal with the nanoparticles larger than 1 nm. Since the shape factor approaches to infinity for nanowires and nanofilms, therefore, the model cannot be generalized to the systems of nanowires and nanofilms. For the input parameters are physical constants of bulk materials, therefore, the present model may be used to predict the lattice variation of different metallic nanoparticles with different lattice structures.

Introduction

It is reported that the lattice parameters of nanoparticles depend on the particle size (Solliard et al., 1985; Lamber et al., 1995; Zubov et al., 1997; Yu et al., 1999; Fukuhara, 2003), which has been reported in experiments (Lamber et al., 1995; Yu et al., 1999) and explained by different models (Solliard et al., 1985; Zubov et al., 1997; Fukuhara, 2003). One characteristic of these theoretical models is that the nanoparticles are regarded as ideal spheres. In most cases, the nanoparticles are spherical; however, the non-spherical nanoparticles (rods-like, disk-like and polyhedral etc.) have also been observed (Link et al., 2000; Simakin et al., 2001) and prepared (Song & Xia, 2002). Since the lattice variation mainly results from the surface effect, therefore, the particle shape should be taken into consideration.

In our previous work, we have developed a model to account for the lattice parameters of spherical nanoparticles (Qi et al., 2002). However, the model is based on the assumption that nanoparticles are formed by changing a macroscopic particle into small nanoparticles. Furthermore, the particle shape is not considered although the concept of particle shape effect on lattice parameters has been mentioned in a comment (Qi et al., 2003).

In the present paper, a modified model will be developed to predict the size and shape dependent lattice parameters, where a metallic nanoparticle is formed in the following way: first, we take out a particle from an ideal bulk crystal without changing the structure; second, the surface tension will contract the particle size a little elastically; third, in equilibrium, the nanoparticle is formed. The particle shape effect on lattice parameters is considered by introducing a shape factor in the present model. By minimizing the sum of the increased surface energy and the elastic energy, we obtain a formula to calculate the lattice parameters of metallic nanoparticles. The calculated lattice parameters of Pd, Au, Cu, Pt, Ag and Al nanoparticles will be compared with the corresponding experimental values.

Model

Taking the shapes of nanoparticles into account, we define a factor α to modify the shape difference between the spherical and the non-spherical nanoparticles (Qi et al., 2003)

$$\alpha = \frac{S'}{S} \tag{1}$$

where S is the surface area of the spherical nanoparticle and $S = 4\pi R^2$. S' is the surface area of the nanoparticle in any shape, whose volume is the same as the spherical nanoparticle. For spherical nanoparticle, we have $\alpha = 1$, and for non-spherical nanoparticle, $\alpha > 1$. Equation (1) can be rewritten as

$$S' = \alpha S \tag{2}$$

The increased surface energy $\Delta\gamma$ after being moved out a nanoparticle from the crystal is

$$\Delta\gamma = \alpha \cdot 4\pi R^2 \gamma \tag{3}$$

where R is the radius of the particles, and γ is the surface energy per unit area at the temperature T ($0 \leq T < T_m$, T_m is the melting temperature of metals). γ can be obtained from the equation given below

$$\gamma = \gamma_0 + T \cdot \frac{\mathrm{d}\gamma}{\mathrm{d}T} \tag{4}$$

γ_0 is the surface energy per unit area at 0 K, and $\mathrm{d}\gamma/\mathrm{d}T$ is the coefficient of surface free energy to temperature. For most solids, we have $\mathrm{d}\gamma/\mathrm{d}T < 0$ (Miedema, 1978).

As mentioned above, the surface energy will contract the nanoparticle elastically. Of course, this kind of contraction is very small compared with the whole particle size. Suppose that a small displacement εR results from this elastic contraction, where $\varepsilon \ll 1$. For spherical particles, the elastic energy f' can be written as the following form according to general elastic theory

$$f' = 8\pi G R^3 \varepsilon^2 \tag{5}$$

where G is the shear module , considering the expression $S = 4\pi R^2$, so we have

$$f' = \pi^{-\frac{1}{2}} G S^{\frac{3}{2}} \varepsilon^2 \tag{6}$$

The elastic energy of a nanoparticle in non-spherical shape is difficult to calculate. However, we can give an approximate estimation by Eq. (6). The parameter ε is the variable, which can be regarded the same for nanoparticles in any shapes. To account for the elastic energy (*f*) of a nanoparticle in non-spherical shape, we should replace S with S' in Eq. (6), then

$$f = \alpha^{\frac{3}{2}} \cdot \pi^{-\frac{1}{2}} G S^{\frac{3}{2}} \varepsilon^2 \tag{7}$$

Equation (7) can be rewritten as

$$f = \alpha^{\frac{3}{2}} \cdot 8\pi G R^3 \varepsilon^2 \tag{8}$$

However, the contraction will make the increased surface energy decrease. Considering contraction effect, the effective increased surface energy is

$$\Delta\gamma = \alpha \cdot 4\pi [R(1-\varepsilon)]^2 \gamma \tag{9}$$

The total energy variation F is the sum of the increased surface energy and the increased elastic energy, which can be written as

$$F = \alpha \cdot 4\pi [R(1-\varepsilon)]^2 \gamma + \alpha^{\frac{3}{2}} \cdot 8\pi G R^3 \varepsilon^2 \tag{10}$$

i.e.,

$$F = A\varepsilon^2 + B\varepsilon + C \tag{11}$$

where

$$A = 4\pi\gamma R^2 \alpha + 8\pi G R^3 \alpha^{\frac{3}{2}}$$

$$B = -8\pi\gamma R^2 \alpha$$

$$C = 4\pi\gamma R^2 \alpha$$

In equilibrium, the total energy is minimum, i.e., $\frac{dF}{d\varepsilon} = 0$, so we have

$$\varepsilon = \frac{1}{1 + \left(\frac{2G}{\gamma}\right) \cdot R \cdot \alpha^{\frac{1}{2}}} \tag{12}$$

For an ideal crystal lattice, the lattice parameter contraction is proportional to the radius of the nanoparticle

Table 1. The input physical parameters

Elememt	Shear module (298 K) $\times 10^{10}$(N/m^2) (Brands, 1983)	Surface energy (0 K) (J/m^2) (Miedema, 1978)	Temperature coefficient of surface energy (J/(K m^2) (Miedema, 1978)	Surface energy[a] (298 K) (J/m^2)
Pd	4.36	2.100	−0.00016	2.052
Au	2.60	1.550	−0.00014	1.508
Cu	4.83	1.850	−0.00019	1.793
Pt	6.09	2.550	−0.00016	2.502
Ag	3.03	1.250	−0.00015	1.205
Al	2.62	1.200	−0.00018	1.146

[a] The surface energy is calculated by Eq. (4).

$$\frac{\Delta a}{a} = \frac{a_p - a}{a} = \frac{(1-\varepsilon)R - R}{R} \tag{13}$$

where a_p and a are the lattice parameters of the nanoparticle and the corresponding bulk material.

Inserting Eq. (12) into Eq. (13), we have

$$\frac{\Delta a}{a} = -\frac{1}{1 + K \cdot D} \tag{14}$$

where D ($= 2R$) is the diameter of the nanoparticle, and $K = \alpha^{\frac{1}{2}} G/\gamma$. Generally, both of the shear module and the surface energy are positive; therefore, the lattice parameter of the metallic nanoparticles will decrease with decreasing of the particle size. Equation (14) is the basic relation for the size and shape dependent lattice parameters of metallic nanoparticles.

Results and discussion

Since the lattice parameters vary with the size and the shape of nanoparticles, we can discuss the particle size effect on lattice parameter in specific shapes and the particle shape effect in specific size. The input parameters are listed in Table 1.

To calculate the lattice parameters of metallic nanoparticles by Eq. (14), it is needed to determine the values of shape factor. Apparently, it is impossible to give all values of the shape factor because we cannot enumerate all possible particle shapes. However, we can give the values of shape factor in some special shapes, which is listed in Table 2.

Table 2. The calculated shape factors for different particle shapes

Particle shape	Shape factor(α)
Spherical	1
Regular tetrahedral	1.49
Regular hexahedral	1.24
Regular octahedral	1.18
Disk-like	> 1.15
Regular quadrangular	> 1.24

For spherical nanoparticles, the shape factor equals 1; for regular polyhedral shapes, the value of shape factor depends on the number of planes. According to Table 1, the shape factor of regular tetrahedral shape equals 1.49, that of cubic shape equals 1.24, and that of regular octahedral shape is 1.18. Apparently, the shape factor approaches 1 with increasing the quantity of planes. Therefore, the values of regular polyhedral shapes range from 1 to 1.49. For disk-like nanoparticles, the value of shape factor depends on the ratio of height to radius. In our calculation, we assume that the radius is 10 times of the height, i.e., the shape factor equals 3.09.

The shape dependent lattice parameters of nanoparticles in specific size have been shown in Figures 1–6. For Pd nanoparticles with 5 nm, the lattice parameter variation equals −0.93% for spherical shape, but −0.80% for regular tetrahedral shape; for Pd nanoparticles with 10 nm, the lattice parameter variation equals −0.48 for spherical shape, but −0.42% for regular tetrahedral shape; similarly, for Pd nanoparticles with 20 nm, the lattice parameter variation equals −0.24% for spherical shapes, but −0.21% for regular tetrahedral shape. Similar results have been obtained for Au, Cu, Pt, Ag and Al nanoparticles. We have the following discussion: (1) the lattice parameter variation depends on the particle size and the particle shape, and the variation decreases

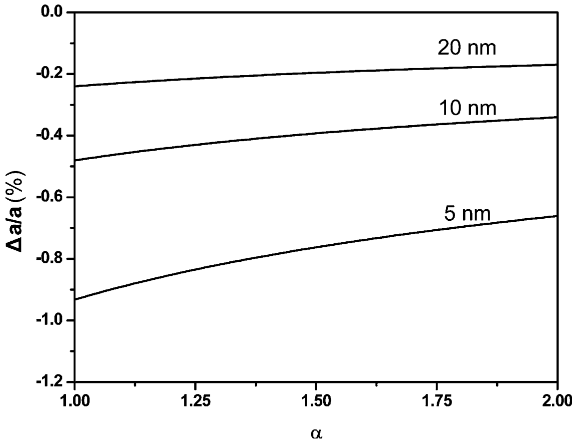

Figure 1. Variation of the relative parameter of Pd nanoparticles as a function of shape factor. The solid lines are the results calculated from Eq. (14).

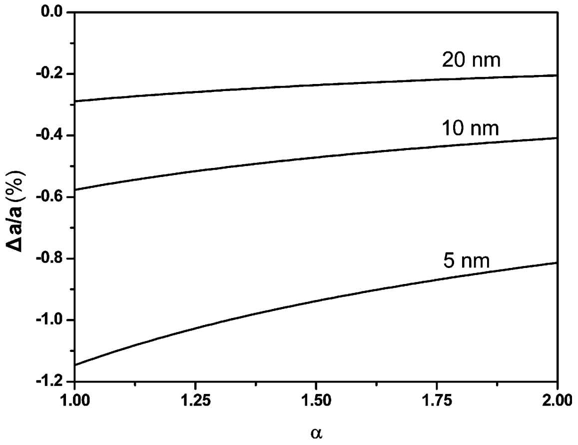

Figure 2. Variation of the relative parameter of Au nanoparticles as a function of shape factor. The solid lines are the results calculated from Eq. (14).

with increasing the shape factor; (2) the smaller the particle size is, the stronger the dependence of lattice parameter to the particle shape is; (3) both the particle shape and the particle size can affect the lattice parameter of nanoparticles, but the particle size is the main factor, and the particle shape is secondary factor. In generally, the particle shape will contribute about 10% to the total lattice variation. In other words, if we ignore the particle shape effect when we calculate the lattice parameters of metallic nanoparticles, the relative error in the final value resulting from the particle shape effect may reach 10%.

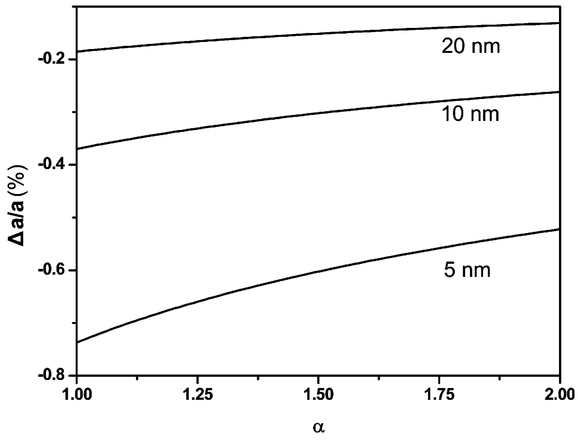

Figure 3. Variation of the relative parameter of Cu nanoparticles as a function of shape factor. The solid lines are the results calculated from Eq. (14).

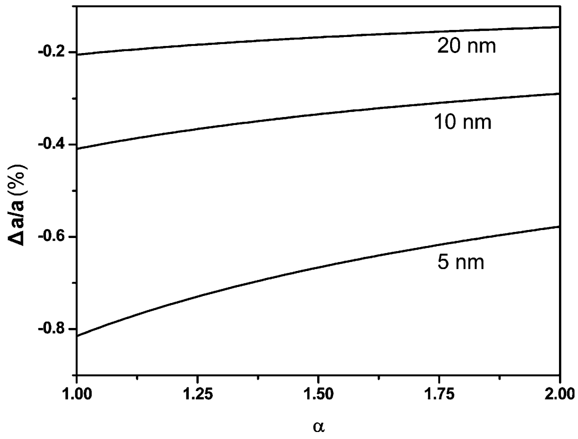

Figure 4. Variation of the relative parameter of Pt nanoparticles as a function of shape factor. The solid lines are the results calculated from Eq. (14).

The size dependent lattice parameters in specific shapes are shown in Figures 7–12. As mentioned above, the lattice parameter variation of spherical, regular tetrahedral and rod-like nanoparticles are plotted, and the corresponding shape factor is 1, 1.49 and 3.09. For Pd nanoparticles, the calculation results by Eq. (14) are consistent with the corresponding experimental values, where the lattice parameters decrease with decreasing the particle size. The experiment values lying in the middle of the two solid lines $\alpha = 1$ and $\alpha = 1.49$ (except for Pd nanoparticle in 2.5 nm) suggest that most of the Pd nanoparticles may be in polyhedral

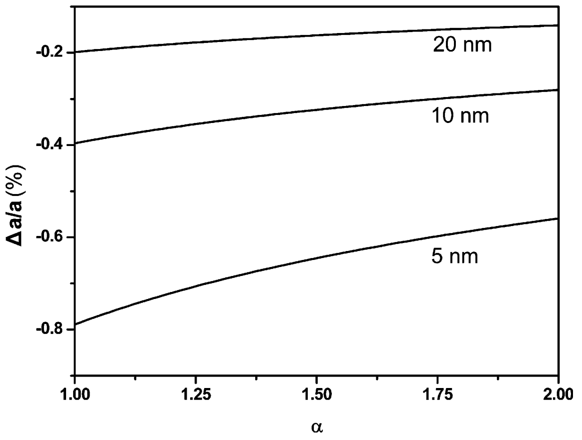

Figure 5. Variation of the relative parameter of Ag nanoparticles as a function of shape factor. The solid lines are the results calculated from Eq. (14).

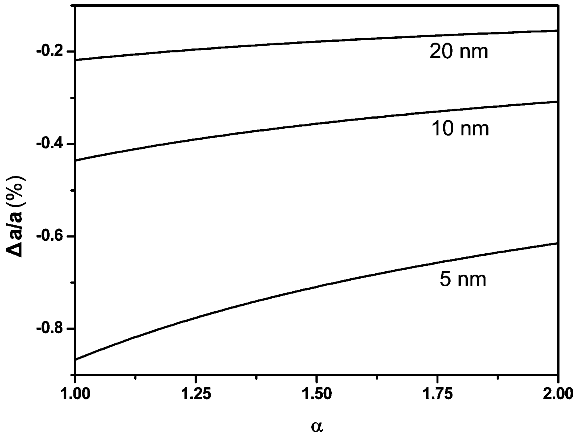

Figure 6. Variation of the relative parameter of Al nanoparticles as a function of shape factor. The solid lines are the results calculated from Eq. (14).

shape, which agrees with definition of shape factor. For Au, Cu, Pt, Ag and Al nanoparticles, the experimental values are close to the theoretical results. The present results show that Eq. (14) obtained in this paper can be used to predict the lattice contraction of metallic nanoparticles. Furthermore, it should be mentioned that the present model is a continuous media model. Therefore, the model can predict the lattice parameters of the nanoparticles whose size is larger than 1 nm, where it is safe to regard nanoparticles as continuous systems. The model can also be tested by further experimental results (the size of nanoparticles should be larger than 1 nm).

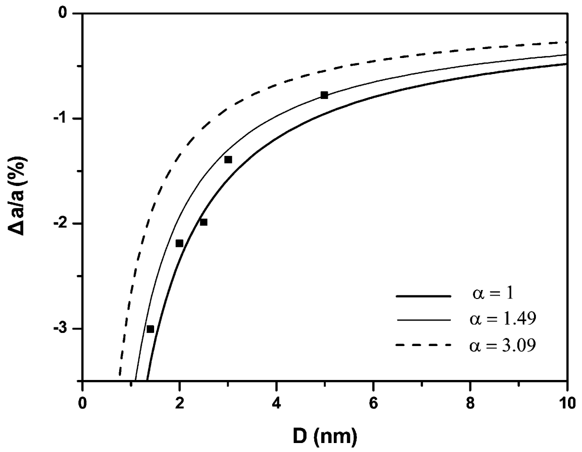

Figure 7. Variation of the relative lattice parameter as the function of the diameter of Pd nanoparticles. The symbols '■' denote the experimental values (Lamber et al., 1995).

According to our model, the metallic nanoparticles are formed by a small elastic contraction after moved out of the bulk material; therefore, it is acceptable to use the values of the shear module of the corresponding bulk metals in our model. Furthermore, it is reported that the surface energy per unit area is independent of the particle size (Alymov & Shorshorov, 1999), therefore, the values of the surface energy per unit area of the corresponding bulk materials have been used. The efficiency of these treatments is confirmed by the calculation results.

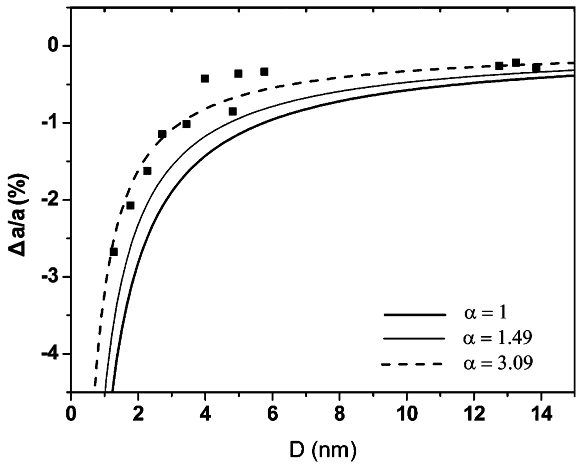

Figure 8. Variation of the relative lattice parameter as the function of the diameter of Au nanoparticles. The symbols '■' denote the experimental values (Mays et al., 1968).

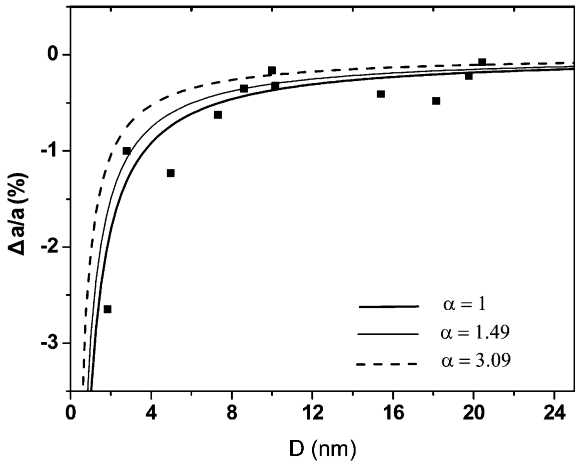

Figure 9. Variation of the relative lattice parameter as the function of the diameter of Cu nanoparticles. The symbols '■' denote the experimental values (Wasserman et al., 1972; Apai & Hamilton, 1979).

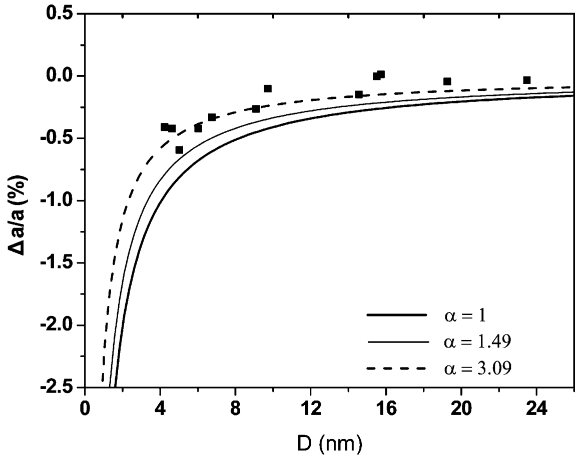

Figure 10. Variation of the relative lattice parameter as the function of the diameter of Pt nanoparticles. The symbols '■' denote the experimental values (Wasserman & Vermaak, 1972).

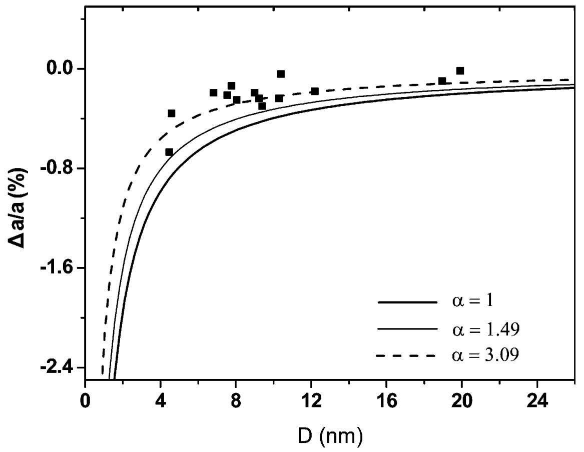

Figure 11. Variation of the relative lattice parameter as the function of the diameter of Ag nanoparticles. The symbols '■' denote the experimental values (Wasserman & Vermaak, 1970).

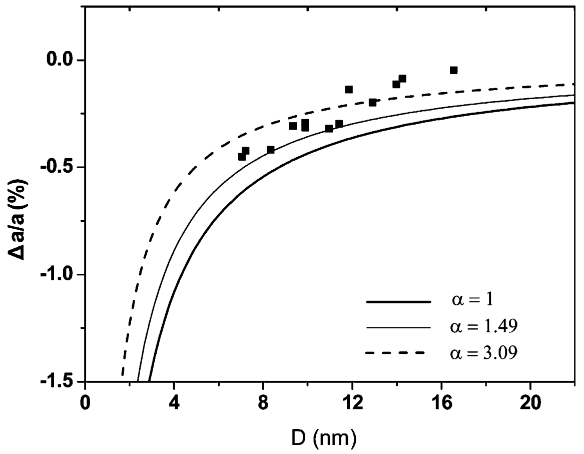

Figure 12. Variation of the relative lattice parameter as the function of the diameter of Al nanoparticles. The symbols '■' denote the experimental values (Woltersdorf et al., 1981).

It should be mentioned that the shape factor can only approximately describe the shape difference between the spherical nanoparticles and the non-spherical nanoparticles. The 'approximately' is stressed here because some non-spherical nanoparticles with different shape may have the identical shape factor, which results from the fact that the shape factor is defined by the surface area. Furthermore, the shape factor is a modified parameter and its value should not be infinite, which means that the present model cannot be used to predict the variation of lattice parameters of nanowires and nanofilms (for nanowires and nanofilms, the shape factor approaches to infinity).

It is reported by some experiments that the small Pd nanoparticles show a dilatation of lattice parameters with decreasing of particle size (Heinemann & Poppa, 1985; Giorgio et al., 1990; Goyhenex et al., 1994), which results from structural change (Giorgio et al., 1990), pseudomorphism (Goyhenex et al., 1994), and incorporation of other atoms such as carbon (Lamber et al.,

1990) and hydrogen (Kuhrt & Anton, 1991) into the particle lattice. These particles are contained by other atoms rather than pure particles, which is out of the scope of our model and will not be discussed here.

Conclusions

A new model is developed to account for the size and shape dependent lattice parameters of metallic nanoparticles, where the particle shape difference is considered by introducing a shape factor. It is predicted that the lattice parameters of Pd nanoparticles in several nanometers decrease with decreasing of the particle size, which is well consistent with the experimental results. Furthermore, it is found that the particle shape can lead to 10% of the total lattice variation. The model is a continuous media model and can deal with the nanoparticles larger than 1 nm. Since the shape factor approaches to infinity for nanowires and nanofilms, therefore, the model cannot be generalized to the systems of nanowires and nanofilms. For the input parameters in present model are the shear module and the surface energy per unit area of the corresponding bulk material, both of which can be obtained easily, therefore, the present new model may be widely used to predict the lattice variation of small metallic particles.

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