



Size Dependence of Lattice Parameters of Spherical Metallic Nanosolids

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ABSTRACT

Variation of lattice parameters depends on the surface energy and the size of nanoparticles. In the present work the model developed by W.H. Qi, and M.P. Wang to predict the size and shape dependence of lattice parameters of metallic nano-particles, has been reviewed in context to the different expressions of surface energy for the nanoparticles of Cu, Au and Pt. I have derived the expression of surface energy for the nanoparticles considering of surface effect with analogy of cohesive energy of nanoparticles. I have used the expression of surface energy with the consideration of broken bonds and surface relaxation, temperature coefficient of surface free energy and the expression of size dependent surface energy derived by me to predict the variation of lattice parameters of nanoparticles. Computed results are compared with the available experimental data from which it is clear that the results obtained for the expression of surface energy derived by me are in good agreement with the experimental results. Main beauty of the suggested expression for the surface energy is that, it is very simple and based on fundamental concept of surface effect. The use of this expression in the model for the prediction of size dependence of lattice parameters reduces the requirement of input parameters therefore; the present expression of surface energy to predict the variation of lattice parameters for different metallic nanoparticles is the most suitable and consistent.

Keywords: Lattice parameters; Metallic nanoparticles; Surface energy; Size dependence of lattice parameters

INTRODUCTION

The size dependence of lattice parameters of nanoparticles has been reported theoretically as well as experimentally [1-6], which are explained by different models suggested by different researchers [1,2,5,7]. In these theoretical models the shape of nanoparticle is regarded as ideal sphere. Usually the nanoparticles are in the shape of sphere but sometimes they may be prepared in the shape of non-spherical nanoparticles like nanorods, nano disk and nano polyhedral etc. [8]. It is observed that the lattice variation is mainly the results of the surface effect, therefore, the particle shape and size should be taken into consideration. A theoretical model has been developed by Qi et al to predict the lattice parameters of spherical nanoparticles as a function of its size [9]. In their model, they have assumed that nanoparticles are formed by changing macroscopic particle into nanoparticles. Further they have also considered that the shape of nanoparticles is same as of macroscopic particle. Considering the different surface dependent physical properties into the consideration Qi et al develop a model to predict the shape and size dependence of lattice parameter for metallic nanoparticles [10]. In this model surface, free energy have an important role to predict the variation of lattice parameters. In their work, they have calculated the surface energy in terms of the coefficient of surface free energy to temperature. Since the cohesive energy has linear dependence of on the surface energy so the dependence of surface energy on particle shape and size will follow same relation as it is in case of cohesive energy. Shiyun et al suggest a model showing the size effects on surface free energy of metallic nanoparticles and nanocavities [11].

In the present work, we suggested a model depicting the variation of surface free energy with the size of nanoparticles with the analogy of its cohesive energy. The expression of surface free energy obtained in this model is used to calculate the size dependent of lattice parameters of nanoparticles alongwith the existing expressions of surface free energy suggested by other group of researchers. Computed results are compared with the experimental values. It is found that our model is most simple and suitable to predict the size dependence of lattice parameters of metallic nanoparticles.

Methods of analysis

Most of the physical properties of nanoparticles depend on the fact that how many numbers of atoms are laying on its surface. There different ways to predict the surface energy of nanomaterials. Since the variation of lattice parameters of nanomaterials depends on the surface energy so the extra attention is required to calculate the surface energy. In the present work authors, have derived a most suitable and simple expression to calculate the surface energy of nanosolids with the analogy to the cohesive energy of nanomaterials. During their derivation authors, have focused on the surface effects of atoms laying on the nanosolids. We have also considered the model suggested for the surface energy of nanoparticles and nanocavities by Shiyun et al [11] with the rigorous consideration of broken bonds and surface relaxation of atoms. The variation of surface energy with the temperature coefficient of surface free energy has also been taken into account to calculate the surface free energy [10]. Model suggested by W.H. Qi and M.P. Wang [10] to predict the variation of lattice parameters of metallic nanoparticles has been used in context to the different expressions of surface energy.

Surface energy with the consideration of surface effect

Let us consider a nanosolid constituted by n number of atoms, out of which N atoms are lying at on its surface. Basically the surface atoms are at the first layer of nanosolid. Now the interior atoms lying below the surface atoms will be $(n-N)$ which behaves as the atoms of bulk materials. Only the surface atoms play crucial role in deciding the properties of nanoparticles. Let γ_0 be the surface energy per atom of the bulk material, then the contribution of interior atoms to the surface energy of nanosolid is $\gamma_0(n-N)$. Since half of the total bonds of each surface atom are dangling bonds so the contribution of each surface atom to the surface energy of the nanosolid will be equal to $\gamma_0/2$. For N number of surface atoms this contribution can be given as $N\gamma_0/2$. Now the total surface energy (γ_{total}) of nanosolid can be given as the sum of the contribution of surface atom and interior atoms, which can be expressed as

$$\gamma_{total} = \gamma_0(n-N) + \frac{1}{2}N\gamma_0 \quad (1)$$

If γ_p is the surface energy per mole of the nanosolid then, it will be equal to the $A\gamma_{total}/n$, where A is the Avogadro constant. Now the equation (1) can be given as

$$\gamma_p = \gamma_b \left(1 - \frac{N}{2n} \right) \quad (2)$$

Where $\gamma_b = A\gamma_0$ is the surface energy per mole of corresponding bulk materials.

In order to correlate the number of atoms with the dimensions nanomaterials let us consider spherical nanosolid of a diameter D . The volume of this specimen can be given as $\pi D^3/6$. The atomic volume of the nanosolid can be written as $\pi d^3/6$; d is the diameters of the atoms constituting the specimen. Now the total number of atoms (n) constituting the nanosolid can be given as the volume ratio of the nanosolid and the atom, i.e.

$$n = \left(\frac{\pi D^3/6}{\pi d^3/6} \right) = D^3/d^3 \quad (3)$$

The surface area of the nanosolid is πD^2 and the contribution of each surface atom to the surface area of the nanosolid is the area of the great circle of the atom, i.e. $\pi d^2/4$. Now the total number of surface atoms can be obtained by the ratio between the surface area of the nanosolid and the area of the great circle of the atom, i.e.

$$N = \left(\frac{\pi D^2 / \pi d^2}{4} \right) = 4D^2/d^2 \quad (4)$$

Now the value of N/n for a spherical nanosolid, can be given as

$$\frac{N}{n} = \left(\frac{4D^2/d^2}{D^3/d^3} \right) = 4d/D \quad (5)$$

Using equation (5) in equation (2) we get

$$\gamma_p = \gamma_b \left(1 - \frac{2d}{D} \right) \quad (6)$$

Surface energy with the consideration of broken bonds and surface relaxation

Shiyun et al suggest a model for surface free energy with rigorous consideration of the broken bonds and surface relaxation [11]. In their findings, they conclude that the surface free energy decreases with particle size. In order to predict this variation required parameters are the diameter of atoms and the surface free energy of the corresponding bulks. Usually the size of the atoms are very less compared to the nanoparticles thus the value of $(d/D)^2$ will be very less and can be ignored in this case, the surface free energy of free nano particles can be further simplified as

$$\gamma_p = \gamma_b \left(1 - \frac{1.45d}{D} \right) \quad (7)$$

Surface energy with the consideration of the temperature coefficient of surface free energy

W.H. Qi and M.P. Wang considered the effect of shape and size of nanoparticles to predict the change in surface energy after being moved out a nanoparticle from the crystal [10]. The increase in surface energy $\Delta\gamma$ can be given as

$$\Delta\gamma = \alpha \cdot 4\pi R^2 \gamma \quad (8)$$

Where R is the radius of the particle and γ is the surface energy per unit area at the temperature T ($0 \leq T < T_m$, T_m is the melting point of the metals) which can be obtained as

$$\gamma_p = \gamma_0 + T \frac{d\gamma}{dT} \quad (9)$$

Where γ_0 is the surface energy per unit area of bulk materials at 0 K and $\frac{d\gamma}{dT}$ is the temperature coefficient of surface free energy.

Size and shape dependent lattice parameters of metallic nanoparticles

W.H. Qi and M.P. Wang [10] derive the expression for the variation of lattice parameters of an ideal crystal lattice and they conclude that the lattice parameter contraction is proportional to the radius of nanoparticles, which can be expressed as

$$\frac{\Delta a}{a} = \frac{a_p - a}{a} = \frac{(1 - \varepsilon)R - R}{R} \quad (10)$$

Where a_p and a are the lattice parameters of the nanoparticles and corresponding bulk materials. The elastic contraction ε for metallic nanoparticles is given as

$$\varepsilon = \frac{1}{1 + \left(\frac{2G}{\gamma_p} \right) \cdot R \cdot \alpha^{1/2}} \quad (11)$$

Where G is the shear module and for spherical nanoparticles $\alpha=1$.

Using equation (11) in equation (10) we get

$$\frac{\Delta a}{a} = -\frac{1}{1+(G/\gamma_p)D} \quad (12)$$

Where, D is the diameter of nanoparticles.

Table 1: Input physical parameters

Element	Shear Modulus (298 K) X $10^{10}(\text{N/m}^2)$ [12]	Surface energy (0 K) (J/m^2) [13]	Temperature Coefficient of surface energy ($\text{J}/(\text{K m}^2)$) [13]	Surface energy (298 K) (J/m^2)#
Cu	4.83	1.85	-0.00019	1.793
Au	2.6	1.55	-0.00014	1.508
Pt	6.09	2.55	-0.00016	2.502

RESULTS AND DISCUSSION

In the present work I, have studied the relative variation of lattice parameters considering the important role of surface energy in the expression proposed by W.H. Qi and M. P. Wang. In order to predict the accurate size dependent variation in the lattice parameters of metallic nanosolids of Cu, Au and Pt we have used the values of surface energies calculated by different expression proposed by different group of researchers [14-16]. I have also derived an expression to calculate the size dependence of surface energy of metallic nanoparticles given in equation (6). During our derivation, I have taken surface effect of nanosolids into the consideration with the analogy of the size dependence of cohesive energy of nanoparticles. Input values are taken from the literature as mentioned in the table-1. I have calculated the values of surface energies by using equation (6), (7) and (9) and used these values in equation (12). Obtained results for the relative variation of the lattice parameters corresponding to different size of Copper, Gold and Platinum nanosolids alongwith experimental values are plotted in the figure(1), (2) and (3) respectively.

From the figure (1) it is observed that the size dependence of experimental values of percentage variation of relative lattice parameters for Copper nanosolids in the size range 2.37 nm to 18.28 nm corresponds from maximum -0.9418% to minimum -0.1191%, (except one value of -1.8227 % at 2.45 nm) [17]. When the calculated values are compared with experimental results it is found that the maximum value of size dependence percentage variation of relative lattice parameters using equation(9), (7) and (6) in equation (12) are -1.5422%, -1.3195% and -1.2163% and minimum values are -0.2027%, -0.2044% and -0.2027% respectively. From this comparison, it is clear that the computed values of size dependent lattice parameters for copper using our model is consistently in good agreement with experimental results.

Similar results are observed in case of gold as shown in figure (2) where the size dependence of experimental values of percentage variation of relative lattice parameters for gold nanosolids in the size range 3.5 nm to 12.5 nm corresponds from maximum -0.4069% to minimum -0.2623% [18]. When the calculated values are compared with experimental results it is found that the maximum value of size dependence percentage variation of relative lattice parameters using equation (9), (7) and (6) in equation (12) are -1.6301%, -1.4567% and -1.3737% and minimum values are -0.4619%, -0.4572% and -0.4505 % respectively. From these results, it is clear that the computed values using equation (6) is very close to the experimental values.

Same observations are pointed out in case of platinum (Pt) shown in figure (3). The experimental values of size dependent lattice parameter for platinum for the size range 3.8 nm to 24.4 nm are available in the literature [17]. Experimental values of maximum and minimum percentage variation in the lattice parameter in case of platinum is -0.8316% and -0.0969% respectively, while the results obtained by using equation (6), (7) and (9) shows that the maximum and minimum values of percentage variation of size dependent lattice parameters for platinum are -0.5180% and -0.0810%, -0.9637% and -0.1682%, -0.9157% and -0.1670 respectively. From these values, it is very much clear that the results obtained through equation (6) are in good agreement with the experimental results.

The expression used for the calculation of size dependence of lattice parameters contains cohesive energy term which is a size dependent quantity [19]. It suggests that the use of size dependent values of cohesive energy in the equation (12) will give more accurate result rather than the fixed values of cohesive energy. The results reported by Qi and Wang [8] based on the fixed values of cohesive energy while I, have taken the size dependent values of cohesive energy. Thus, our results are in good agreement than the results reported by others. On the basis of above discussion about the findings it seems that the size dependence of cohesive energy plays an important role for the prediction of variation in the lattice parameters of metallic.

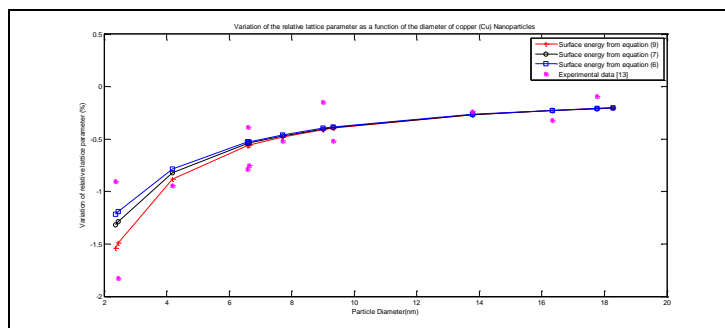


Figure1: Variation of relative lattice parameters as a function of the diameter of Copper (Cu) nanosolid

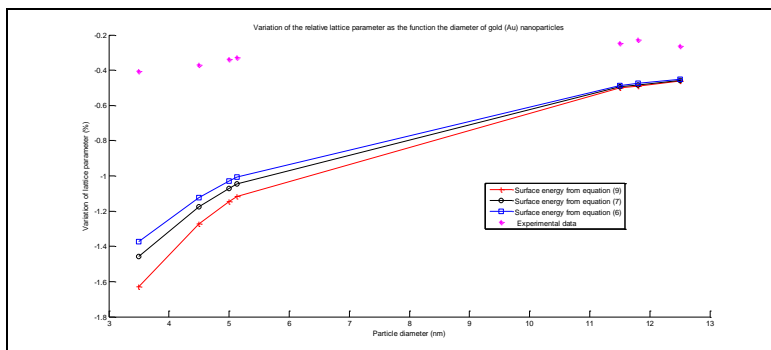


Figure 2: Variation of relative lattice parameters as a function of the diameter of Gold (Au) nanosolid

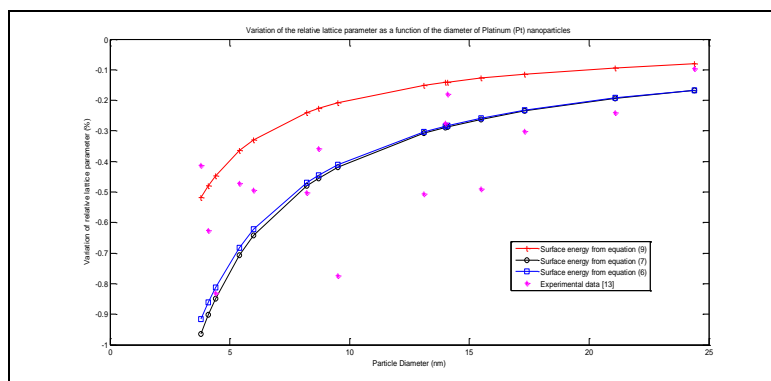


Figure 3: Variation of relative lattice parameters as a function of the diameter of Platinum (Pt) nanosolid

CONCLUSION

Size and shape dependence of lattice parameters of metallic nano-particles, has been reviewed in context to the different expressions of surface energy for the nanoparticles of Cu, Au and Pt. The expression used for the calculation of size dependence of lattice parameters contains cohesive energy term which is a size dependent quantity [17], which suggests that the use of size dependent values of cohesive energy in the equation (12) will give more accurate result rather than the fixed values of cohesive energy. I, have taken the size dependent values of cohesive energy to predict the size dependence of lattice parameters while others calculations are based on the fixed values of cohesive energy. Thus our results are in good agreement with experimental values than the results reported by others. On the basis of above discussions it is clear that that the size dependence of cohesive energy plays an important role for the prediction of variation in the lattice parameters of metallic nanosolids, and hence it must be considered for the prediction of variation in lattice parameters of metallic nanosolids.

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