National University of Lesotho International Science, Technology & Innovation Conference & Expo
January 23 – 25, 2018
Maseru, Lesotho
nulistice 2018

Modelling of Thermal Expansion Coefficient and Specific Heat of Nanomaterials

M. Singh

Department of Physics & Electronics, National University of Lesotho, Roma 180, Lesotho

Corresponding author: Phone: (+266) 5221 3531; E-mail: m.singh@nul.ls

Abstract: The size effect is fuelled by increasing the fraction of the surface atoms with lower coordination numbers, consequently increasing number of dangling bonds, which results in effecting the thermodynamical properties as cohesive energy, melting point and specific heat at nanoscale. The cohesive energy of nanoparticles decreases due to the dangling chemical bonds. On considering the surface effect, a simple model is discussed to study the size and shape dependence physical properties of nanomaterials. A simple model is discussed to study the size dependence of thermal expansion coefficient and specific heat of Ag and Ni nano sized solids with different shapes. Here, a shape factor is introduced, which is defined by ratio of surface area of non-spherical nanosolid to the surface area of nanosphere. It is predicted that the thermal expansion increases with decrease in particle size. It is realized that the particle shape can influence the thermal expansion of nanoparticles and this effect on the thermal expansion becomes larger with decreasing of particle size. On the same ground, I extended this model to analyse the specific heat of the nanomaterials. It is reported that our specific heat increases as particle size decreases. Our theoretical predictions agree fairly well with the available experimental and simulation results for nanosized particles in different shapes.

Keywords: Nanosphere, Particle shape, Nanofilm, Nanosolid, Nano materials

1. Introduction

Nanostructure science and technology is one of the broad and multidisciplinary fields of research in material science. Nanostructured materials comprise atomic clusters, threadlike structures, layered films and bulk nanocrystalline materials. Physics of nanomaterials is unlike from its macroscopic material and their properties are usually notable due to which nanomaterials are of vigorous research importance. Using different approaches of blend, it is possible to tune their thermodynamic properties. The thermodynamic properties are induced with the change of size as well as shape [1-2]. The cohesive energy is basic physical measure to define the strength of bond [3]. It is constant for bulk materials. But, for nanomaterials their cohesive energy depends upon on the size of the nanomaterials, which has been showed by experiments and also explained by different theories such as liquid drop model [4], surface area difference model and bond energy model. The vital idea is that the atomic cohesive energy controls the thermodynamic properties with the atomic coordination nature. The bond theory model describes how the surface dangling bonds changes the properties of nanoscale materials [5]. The thermodynamic properties of silver nanoparticles are reviewed like melting temperature, molar heat of fusion, molar entropy of fusion and temperature dependence of entropy and specific heat [6]. The findings reveal that these thermodynamic properties can be divided into two parts such as bulk quantity and surface quantity; also surface atoms dominate for the size effect on the thermodynamic properties of nanomaterials. The heat capacity of ideal nickel, copper, gold, aluminum and palladium fcc clusters with diameter up to 6 nm has been studied in terms of the molecular dynamics theory using a tight binding potential [7].

Thus, an analytical study of the literature reveals that a lot of experimental work has been done allied to the size dependence of thermal expansion and specific heat. Although, the theoretical works are lacking. Some efforts, based on potential approach and simulation made by earlier workers, are grounded on several approximations which involve tedious computations and are time overwhelming. It is a very tough task to extend the potential based approach for complicated solids. In the present work, I used the bond energy model [8] and reported a very simple and authentic method to study the effect of size and shape on thermal expansion coefficient and specific heat of nanomaterials.

Table 1. Input data used in calculations

Shape of cross section	Spherical	Film	Regular tetrahedral	Regular hexagonal
Shape factor	1	1.15	1.49	1.24

2. Materials and Methods

Bond energy is the measure of bond strength. The sum of bond energies of all the atoms is expressed as the cohesive energy of metallic nanoparticles. The cohesive energy of a solid is defined as the energy required in breaking the atoms of the solids into isolated atoms. Since half of the total bonds of each surface atom are dangling bonds, according to the bond energy model, the cohesive energy of nanoparticles is the summation of contribution of inner shell and outer shell atoms, which are defined as $E_{cn} = E_{cb}\left\{1-(\gamma N/n)\right\}$ [8]. Where n and N are the total number of atoms and surface atoms of nanosolids respectively. Here, γ is the relaxation factor, which is defined as the ratio between the dangling bonds and the total bond of the atoms. Agreeing that the number of bonds is proportional to the surface area, one can write $\gamma = S'/S$. Here, S' is the surface area with dangling bonds and S is the entire surface area of the atom. In the low dimension of nanosolids, the different position of atoms are discussed [5] and reported the value of γ may have the following 0, ¼, ½, 3/4 and 1. Thus, the relaxation factor is in the range of $0 \le \gamma \le 1$. The value of N/n can be calculated using the concept of surface area to volume ratio as $N/n = 4\eta d/D$. Where, η is the dimensionless shape factor which is defined by the ratio of nanoparticle in any shape whose volume is the same as spherical nano particle to the area of spherical nanoparticle. Here, d is the diameter of nanoparticle. It is reported that the cohesive energy has a linear relation with the melting temperature of the solids [9]. Therefore, the size and shape dependent melting temperature of nanomaterials should follow the similar relation given as

$$T_{mn} = T_{mb}\left\{1-(\gamma 4\eta d/D)\right\} \qquad (1)$$

It is listed [10] that the size and shape dependent thermal expansion coefficient of nanomaterials as $\alpha_{mn}/\alpha_{mb} = T_{mb}/T_{mn}$. Consequently, from equation (1) one can get the thermal expansion coefficient of nanomaterials as

$$\alpha_{mn} = \alpha_{mb}\left(1-\gamma\frac{4\eta d}{D}\right)^{-1} \qquad (2)$$

Where, α_{mb} is the thermal expansion coefficient of corresponding bulk materials. Xiong et al. [11] disclosed that specific heat increases as the particle size decreases. The increased specific heat is caused by the atomic thermal vibrational energy of the surface atoms. On this ground, theory is extended to study the specific heat of nanomaterials in different sizes and shapes. It is presented the specific heat of nanomaterials as

$$C_n = C_b\frac{1}{1-\gamma\dfrac{N}{n}} \qquad (3)$$

3. Results and Discussion

The input parameters [11-12] required for the present work are given in Table 1-2. Variation of thermal expansion coefficient and specific heat of Ag and Ni nanomaterials has been calculated by eq. (2) and (3) respectively. In this work, nanosolids are selected in four different cross sectional shapes like spherical, film, regular hexagonal and regular tetradedral. The graphical representations of the calculated results of thermal expansion coefficient are shown in figs. (1 and 2). It is observed that the thermal expansion coefficient increases on increasing the size of the nanoparticles, which indicates that the strength of metallic bond of nanomaterialds is weaker than that of bulk metal. It is reported that the thermal expansion coefficient is maximum for regular tetragonal shape and minimum for spherical shape. This behaviour can be clarified on the origins of the bond energy model of cohesive

Table 2. Input data used for calculations [11, 12]

Nanomaterials	d(nm)	α_{mb} ($10^{-5}/K$)	C_b (J/Mol/K)
Ag	0.319	1.8	25.35
Ni	0.249	3.3	26.07

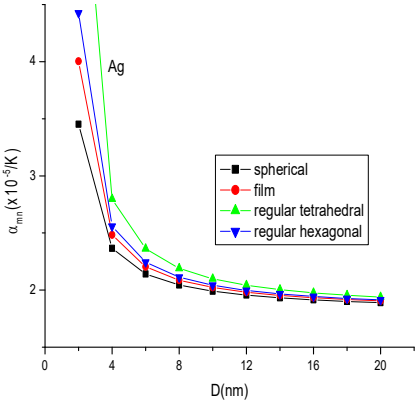

Figure 1. Particle size dependent thermal expansion coefficient of Ag nanosolid in spherical, film, tetrahedral and hexagonal shapes.

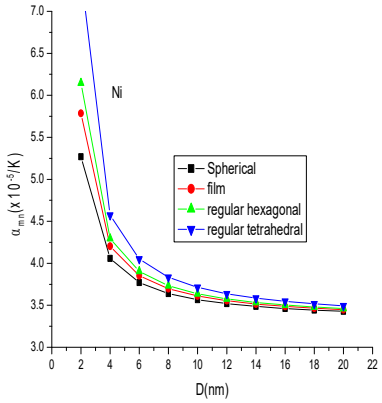

Figure 2. Particle size dependent thermal expansion coefficient of Ni nanosolid in spherical, film, tetrahedral and hexagonal shapes.

energy, which differs with shape and size of nanomaterials. As the particle size reduces, surface to volume ratio of the nanomaterials rises. Thus, the number of dangling bonds increases and consequently cohesive energy decreased. The model is extended to study the specific heat of Ag and Ni nanomaterials. Using equation (3), the size and shape dependence specific heat is calculated of Ag and Ni nanomaterials. The computed values of specific heat of Ag and Ni nanosolids are shown in figs. (3-4) along with available experimental data [12]. It is observed that the specific heat increases with decrease in particle size. To account for the shape of the cross section, shape factor is incorporated and it is clearly confirmed by this study that thermodynamical properties are not only a size dependent but also depends on the shape. There is a good agreement between the model and the available experimental findings, which validates the fitness of the model suggested for specific heat. The increased nature of specific heat can be explained on the basis of the electron and phonon contribution to specific heat. In nanostructure, phonons usually dominate and the phonon properties of the structure become a particular importance for specific heat. Since, phonon-phonon interaction increases with reduction due to the confinement, which causes the increase of thermal resistance and decrease of thermal conductivity, consequently increases the specific heat. In this theory, the shape factor is used to explain the shape effects of the nanosolids; though, the different influences of the edge, corner, and the face atoms to the cohesive energy are not taken in account.

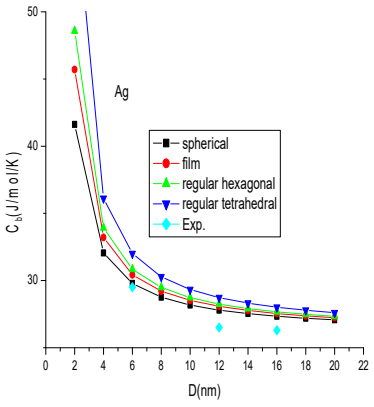

Figure 3. Particle size dependent specific heat of Ag nanosolid in spherical, film, tetrahedral and hexagonal shapes. Exp. data [12] shown by points ♦.

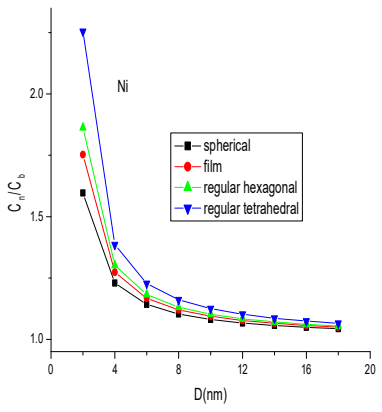

Figure 4. Particle size dependent specific heat of Ni nanosolid in spherical, film, tetrahedral and hexagonal shapes.

4. Conclusions

In the present work, I have discussed the simple and straight forward theory based on bond energy model, free from approximation to calculate the thermal expansion and the specific heat of Ag and Ni nanomaterials in different shapes and sizes. It is reported that the thermal expansion and specific heat increases with decrease in size. Additionally, it is also reported that the thermal expansion and specific heat also changes with the shape of the nanomaterials and its value is larger for regular tetragonal and minimum for spherical shape. Results reported are compared with the available experimental data and shown that findings are reasonable consistent with the corresponding experimental values.

5. References

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