

Modeling shape and size dependence of thermal expansion and Debye temperature of nanocrystals

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Abstract

A simple theoretical model is developed to explore the size and shape dependence of thermal expansion and Debye temperature of nanomaterials. The model theory is based on cohesive energy and surface area change of the nanocrystals compared to the bulk crystals. It is found that the Debye temperature decreases with the decrease in particle size whereas, the thermal expansion increases as the particle size decreases. The present modelling results and predictions are very consistent with the available experiment results, implying that the model could be expected to be a general approach to understand the thermodynamic properties of nanomaterials. Copyright © 2017 VBRI Press.

Keywords: Nanomaterials, Debye temperature, thermal expansion, thermodynamic properties, surface energy.

Introduction

Nanotechnology mainly consists of the processing of separation, consolidation and deformation of materials by one atom or by one molecule. Nanotechnology and nanoscience began in the early 1980's with the advances in computing power and material modelling. A link between the depressions of the melting temperature and the Debye Temperature in metal nanowires was developed and check the validity of Lindeman relation on size reduction that connects these two physical quantities [1].

When the grain size of materials changes the nanometre scale, optic, electronic, magnetic, catalytic, biomedical and thermodynamic properties vary noticeably from those of an isolated atom and bulk materials [2-4]. It is recognized that the size dependence of thermal stability in nanomaterials is gradually becoming one of the major interests in upcoming technologies [5]. Cohesive energy, which is defined as the difference between the average energy of the atoms in a solid and the isolated atoms, is one of the most important physical parameters in quantifying the thermal stability of materials [6, 7]. Many experimental and theoretical efforts have been implemented to investigate the size-dependent cohesive energy of nanomaterials [8, 9]. At nanoscale Ag and Au have demonstrated many interesting chemical and physical properties that their bulk counterparts do not have. Liu *et al.* [10] have obtained

such a model that is capable to reunite the observed size dependence of the lattice strain, core level shift, elastic modulus, and thermal stability of Au and Ag nanostructures from the perception of skin-depth bond order loss. For bulk materials, the surface effect can be neglected for most thermodynamic properties, however, surface effect cannot be ignored for nanomaterials. Surface effects results from the difference between the surface atom and inside atoms, the surface atoms are less stable than the inside atoms due to their less coordination number than that of inside atoms. The ratio of surface atoms to the total atoms is relatively large, which indicates to the size dependence of the thermodynamic properties of nanomaterials.

In this paper, we register a theoretical model without adjustable parameters based on cohesive energy and surface effect for studying the particle size and shape dependent thermal expansion coefficient and Debye temperature of Sn, Pb, and Au nanosolids for spherical nanoparticles, nanowires, and nanofilms. It is found that the present model has good consistency with the available experimental data. The study established on cohesive energy and surface effect at decreased particle size, permits interpolation and extrapolation to the region for which adequate experimental data are not available. To the best of my knowledge this is the simple method to calculate the thermodynamic properties of the nanomaterials.

Experimental

Theoretical formulation

The cohesive energy of the nanomaterials is the sum of energy due to the contributions of the interior atoms and the surface atoms, which is expressed as [11].

$$E_{sum} = E_0(n - N) + \frac{1}{2}E_0N \quad (1)$$

where, n is the total number of atoms of nanosolids and the number of its surface atoms is N .

Therefore, $(n - N)$ is the total number of interior atoms of the nanomaterials. E_0 is the cohesive energy of the bulk materials per-atom. Eq. (1) may be written as

$$E_p = E_b \left(1 - \frac{N}{2n}\right)$$

where, E_p is the cohesive energy per mole of the nanomaterials, which is given by $\frac{AE_{sum}}{n}$, here, A is the

Avogadro constant. E_b is defined as the cohesive energy per mole of the corresponding bulk materials which is given by $E_b = AE_0$.

The relation between the melting point of nanomaterials and bulk are reported by Qi [11] as:

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

One may get the connection between the melting point and the Debye temperature from the Lindemann's comparative. According to this, a crystal will melt when the root mean square displacement of an atom exceeds a certain fraction of the interatomic distance in the crystal [12]. Relating the specific heat theory with the Lindemann's melting formula, the characteristic temperature square is proportional to the melting point of the crystal. So, the Debye temperature for the bulk material is inscribed as [13].

$$\theta_b^2 \propto \left(\frac{T_b}{MV^{2/3}}\right) \quad (3)$$

Equally for nanomaterial

$$\theta_p^2 \propto \left(\frac{T_p}{MV^{2/3}}\right) \quad (4)$$

where, M is the molecular mass.

Equations (3) and (4) give the following relation we get

$$\left(\frac{\theta_p^2}{\theta_b^2}\right) = \frac{T_p}{T_b} \quad (5)$$

Kumar [14] derived the relation for α_p , which is recited as

$$\alpha_p = \alpha_b \left(1 - \frac{N}{2n}\right)^{-1} \quad (6)$$

Therefore, from Eq. (5) and (6) one can get

$$\left(\frac{\theta_p}{\theta_b}\right) = \left(1 - \frac{N}{2n}\right)^{1/2} \quad (7)$$

where, N is the total number of surface atoms and n is the total number of nanosolids. α_b is coefficient of volume thermal expansion of bulk material. The surface atoms refer to the first layer of the nanosolid. The method to find $N/2n$ for different shape of nanomaterials has been debated by Qi [11]. The value of $\frac{N}{n}$ is $\frac{4d}{D}$, $\frac{8d}{3l}$ and $\frac{4d}{3h}$ for spherical nanosolids, nanowires and nanofilms respectively [11]. Where, d is the diameter of the atom of nanosolid and D is the diameter of the spherical nanosolids. l and h are the diameter of nanowire and height of the nanofilm correspondingly.

Table 1. Input parameters [15, 16, 17].

Nanomaterials	d(nm)	Debye temperature
		θ_b (K)
Sn	0.372	-
Pb	0.386	-
Au	0.288	184.5

Results and discussion

The input parameters [15, 16, 17] required for the present work are given in **Table 1**. We used Eqs. (6) and (7) for the calculation of thermal expansion and Debye temperature of Sn, Pb and Au nanomaterials in different shapes, namely, spherical nanoparticle, nanowire and nanofilm. The results are reported in **Fig. 1-5** respectively along with the available experimental data [18]. Eq. (6) is used to study the size and shape dependence of thermal expansion of Sn, Pd and Au. The calculated values of thermal expansion of Sn, Pd and Au in spherical, nanowire and nanofilm shapes are shown in **Fig. 1-3**. The thermal expansion is found to increase with the decrease in the particle size. The trend of variation is similar in all three forms. Moreover, the thermal expansion increases less for nanowire and nanofilm as compared to the spherical form of the same size.

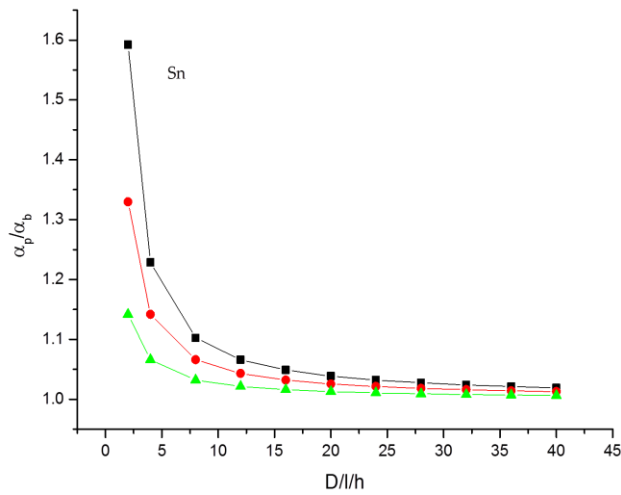


Fig. 1. Size dependence thermal expansion coefficient ratio of Sn (nanosphere, nanowire and nanofilm) obtained Eq. (6). The lines with symbols square, circle and triangle are for nanosphere, nanowire and nanofilm, respectively.

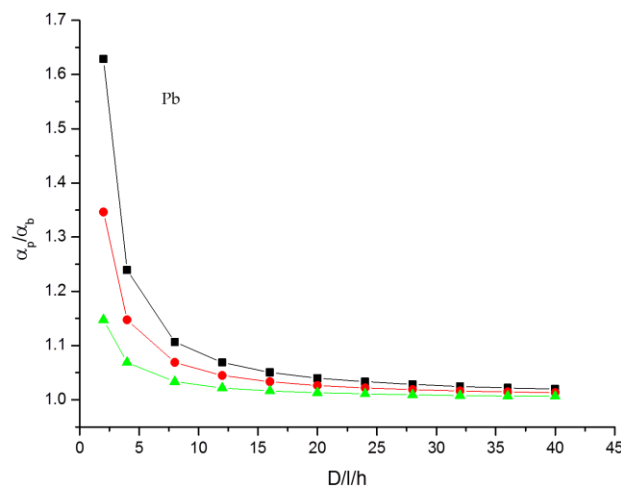


Fig. 2. Size dependence thermal expansion coefficient ratio of Pb (nanosphere, nanowire and nanofilm) obtained Eq. (6). The lines with symbols square, circle and triangle are for nanosphere, nanowire and nanofilm, respectively.

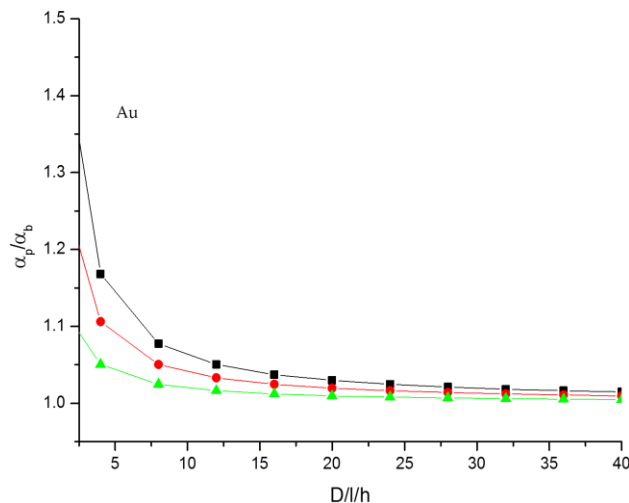


Fig. 3. Size dependence thermal expansion coefficient ratio of Au (nanosphere, nanowire and nanofilm) obtained Eq. (6). The lines with symbols square, circle and triangle are for nanosphere, nanowire and nanofilm, respectively.

The Debye temperature variations of Au, calculated by Eq. (7) are reported in **Fig. 4**. It is found that Debye temperature decreases with decrease in particle size. For the sake of comparison of Au (spherical nanosolid), the experimental values [18] are shown in the **Fig. 4** by solid dots, which support well to our calculated results. This added the validity of the model exercised. A good agreement between theory and experiment for the size and shape dependence of Debye temperature encouraged the authors to extend the theory for the Pd nanomaterials in different shapes.

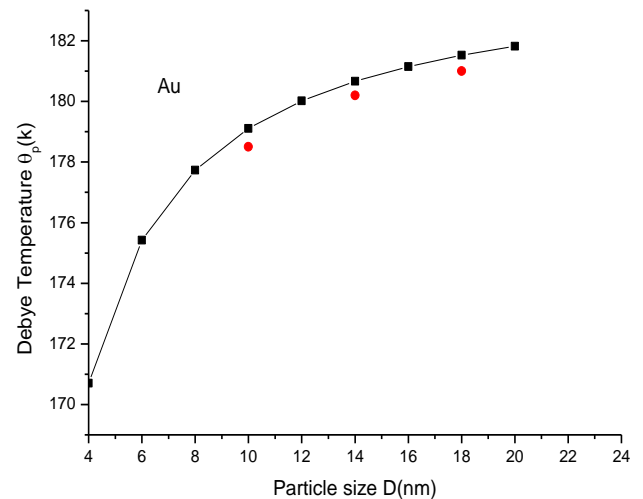


Fig. 4. Size dependence Debye temperature of Au spherical nanosolid. Solid line with squares is our theoretical value obtained by Eq. (7). Solid dots are the experimental values [18].

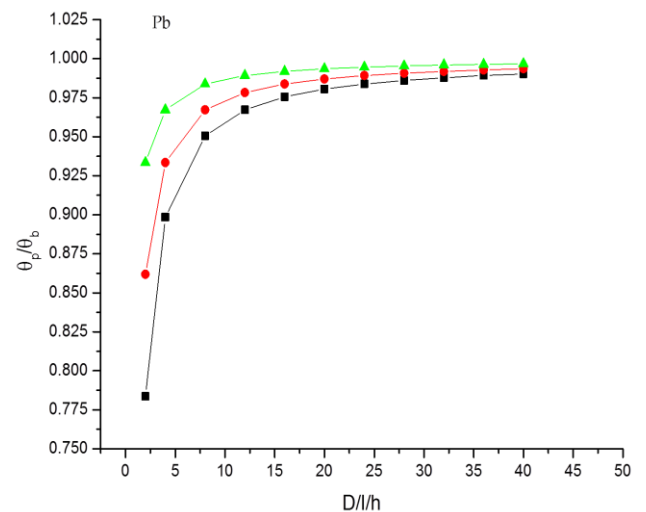


Fig. 5. Size dependence Debye temperature ratio of Pb (nanosphere, nanowire and nanofilm) obtained Eq. (7). The lines with symbols square, circle and triangle are for nanosphere, nanowire, and nanofilm, respectively.

Fig. 5 is the size dependent Debye temperature of Pb nanoparticles computed using Eq. (7). It is found that the Debye temperature decreases with decrease in particle size. Moreover, there is increase in the Debye temperature from spherical to nanowire to nanofilm for the particular

size. The fact is that, by decreasing the particle size, the more and more portion of atoms occupies surface area, and these are dangling atoms which are able to move freely. This phenomenon reports to change in the thermodynamic properties of the nanomaterials.

The experimental values for the size dependence thermal expansion of the given nanosolids do not exist in the text. Although, the trend of variation is similar to that obtained Debye temperature. Which support that temperature is inversely proportional to the thermal expansion. These findings may be of kind attention to the scholars involved in the experimental analyses of size dependence thermal expansion.

Conclusion

Size dependence thermal expansion and Debye temperature of nanomaterials in different shapes (nanosphere, nanowire and nanofilm) have been studied. It is shown that the calculated results of Debye temperature and thermal expansion of Sn, Pb and Au nanomaterials are consistent with the available experimental results. Also, it is found that the particle shape affects the Debye temperature and thermal expansion of the nanomaterials. The effect on Debye temperature and thermal expansion become more with the reducing of particle size. The method presented in this paper may have potential application to find the size dependent thermodynamical properties of nanomaterials.

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