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Analysis of Size and Shape Dependence of Thermophysical Properties of Nanomaterials

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Abstract

A simple qualitative model, named Qi model which is further extended to Bond energy model has been expressed in terms of melting temperature to explain the shape and size effect on Debye temperature (θ_{Dn}) *and Einstein temperature* (θ_{En}) *of nanomaterials. It is known that properties of materials drastically change with size reduction to nanorange and increase in the number of surface atoms with respect to volume of the nanostructure. It is found that Debye temperature and Einstein temperature get reduced in free standing nanostructures as their size is reduced. The variation in these physical properties viz. Debye temperature* (θ_{Dn}) *and Einstein temperature* (θ_{En}) *is calculated for spherical nanoparticles, thin film, and nanowires for considered nanomaterials. The computed results are compared with the available experimental results and it is found that there is a good agreement between them. The results obtained for the bulk materials are also depicted in the graphs to judge the stability of this work.*

Keywords: Debye temperature, Einstein temperature, size, shape, nanowire

INTRODUCTION

Study of nanomaterials is of great interest in today's era because of the applications of nanomaterials on a large scale. It is known that nanomaterials are characterized by a large number of atoms which are present on their surface as compared to the atoms on their volume which modify various types of properties of nanomaterials i.e. mechanical, chemical, physical, elastic and thermodynamic properties [1-5]. The study of nanoscience and nanotechnology is a very active and challenging from few decades. Among all properties of nanomaterials, the Debye temperature is one of the most important properties because it is used as a basic building block to do the calculation for other properties of nanomaterials [6-9]. Many types of methods i.e. experimental, simulation, and theoretical are available to discuss the characteristics of nanostructures. The properties of nanomaterials can be done using either top down approach or bottom up approach. In Bottom up approach, simulation techniques are used that involve complex computational work and in top down approach, classical thermodynamics is used. Moreover, some physical properties like thermal expansion coefficient, Einstein temperature, and specific heat are related to Debye temperature [10-12]. The expression of thermal conductivity can also be derived with the help of specific heat formula. Many experimental and theoretical studies have been performed by many scientists to study the properties of nanomaterials.

Yang et al. [13] explains the effect of size on volume thermal expansion coefficient, Einstein temperature, and Debye temperature of nanomaterials and Gafner et al. [14]. analyze the heat capacity of nanoclusters. From previous studies, it is noticed that Debye temperature and

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Einstein temperature are depressed as the size of nanomaterials is reduced. It is noted from previous studies that the thermodynamical properties of nanomaterials are intrinsically dependent on binding energy that is linearly proportional to the melting temperature of the material.

This model required to predict the physical properties of nanomaterials must require less number of input parameters. In this work, the author have analyzed the size and shape effect of some physical properties i.e. Einstein temperature (θ_{En}) and Debye temperature (θ_{Dn}) of nanomaterials by using Bond energy model [15]. The nanoparticles taken in this theoretical study are Se, Au, Co, and Cu. The variance in these properties with size is studied theoretically for spherical shape, thin film, and nanowire shapes. A comparison of computed results has been done with the experimental data which are present in literature. The methodology used is described in section 2 and the discussion of the results obtained is done in section 3. A nice consistency is obtained between the calculated and experimental results indicate the superiority of our theoretical work.

METHODOLOGY

Melting Temperature

The melting temperature of nanomaterials can be expressed by using Bond energy model [15]. as follows:

$$\frac{T_{mn}}{T_{mb}} = \left(1 - \frac{N}{2n}\right)^{k} \qquad (1)$$

Where T_{mn}, T_{mb} denotes the melting temperature for nanomaterials as well as bulk materials, N represents the atoms which are on the surface, n indicates the total number of atoms, and k is the dimensionless quantity which may have different values. Its value can be negative, zero, and may be a positive number. Values of k taken here are 0, 1, 2, and 3 respectively. For k=0 the material with no size effect behaves as a bulk material and for k=1 equation (1) becomes the expression of Qi model.

Debye Temperature

As, melting temperature and Debye temperature are related as given by Liang and Baowen [16]:

$$\frac{T_{mn}}{T_{mb}} = \frac{{\theta_{Dn}}^{2}}{{\theta_{Db}}^{2}} \qquad (2)$$

Where, θ_{Dn}, and θ_{Db} denotes the Debye temperature for nanomaterials as well as bulk materials.

$$\frac{\theta_{Dn}}{\theta_{Db}} = \left(\frac{T_{mn}}{T_{mb}}\right)^{1/2} \qquad (3)$$

Now substituting the value of $\frac{T_{mn}}{T_{mb}}$ from equation (1) in equation (3) as follows:

$$\frac{\theta_{Dn}}{\theta_{Db}} = \left(1 - \frac{N}{2n}\right)^{k/2} \qquad (4)$$

The value of $\frac{N}{2n}$ are $\frac{4d}{3L}$, $\frac{2d}{3h}$, and $\frac{2d}{D}$ for nanowire, thinfilm, and sphere shapes respectively [17]. Where d, L, h, and D represents the atomic diameter, length, height, and diameter of nanomaterials.

For 1-D, 2-D, and 3-D nanomaterials equation (4) can be written as:

$$\frac{\theta_{Dn}}{\theta_{Db}} = \left(1 - \frac{4d}{3L}\right)^{k/2} \qquad (5)$$

$$\frac{\theta_{Dn}}{\theta_{Db}} = \left(1 - \frac{2d}{3h}\right)^{k/2} \qquad (6)$$

$$\frac{\theta_{Dn}}{\theta_{Db}} = \left(1 - \frac{2d}{D}\right)^{k/2} \qquad (7)$$

Einstein Temperature

Since Einstein temperature (θ_{Eb}) varies in the same proportion as Debye temperature (θ_{Db}) [18]. So, the Debye temperature expression can be extended to obtain Einstein temperature in the case of nanomaterials as follows:

$$\frac{\theta_{En}}{\theta_{Eb}} = \left(1 - \frac{N}{2n}\right)^{k/2} \qquad (8)$$

Einstein temperature for nanowire, nano film, and sphere shape nanomaterials can be expressed as follows:

$$\frac{\theta_{En}}{\theta_{Eb}} = \left(1 - \frac{4d}{3L}\right)^{k/2} \qquad (9)$$

$$\frac{\theta_{En}}{\theta_{Eb}} = \left(1 - \frac{2d}{3h}\right)^{k/2} \qquad (10)$$

$$\frac{\theta_{En}}{\theta_{Eb}} = \left(1 - \frac{2d}{D}\right)^{k/2} \qquad (11)$$

RESULTS AND DISCUSSION

In this theoretical study, the effect of shape and size on the physical properties viz. Debye temperature (θ_{Dn}) and Einstein temperature (θ_{En}) of nanosolids has been discussed with the help of Bond energy model. The necessary input parameters required in the present work are listed in table 1. Debye temperature variation with shape and size of nanomaterials is computed by using equation 4 and variation of Einstein temperature is studied by using equation 8 respectively. The Debye temperature and Einstein temperature are considered in Kelvin and size of the nanomaterial varies from 2-30 nm. Value of k taken here are 1, 2, and 3 and also the results for bulk materials are also considered here for the comparison purpose.

Table 1. Necessary input parameters required in the present work [19-23]:

S. no	Nanomaterial	d (nm)
1	Se	0.4366
2	Co	0.251
3	Au	0.288
4	Cu	0.256

Debye temperature variation with size for Se nanostructure with spherical shape for all values of k is shown in Figure 1. Experimental results computed by Zhao et al. [24] are inserted in the graphs to judge the suitability of our present work. It is found that a good consistency of computed results is with experimental results. Figure 2 represents the Debye temperature variation with size for Co nanosphere with different values of k. The experimental results given by Hou et al. [25] are very close to the computed results for k=2. For gold nanomaterial the size effect on Debye temperature for considered values of k in shown in figure 3. It is found that the experimental data are very near to the computed results for k=3. For copper nanomaterial the Debye temperature variation with size for shapes is shown in figure 4 for k=0,1,2, 3Experimental data of relative Debye temperature variation in Cu nanostructures is not available but it is noticed that the variation trend is same as observed in previous studies. A good agreement of calculated results with experimental data for all nanomaterials is observed in this theoretical work. It is also observed that computed data for relative Debye temperature variation with size is deviated from experimental value available for certain sizes because the present model has not taken into account all the parameters such as pressure temperature conditions, impurities in material, crystal structure at specific size during experiment etc.

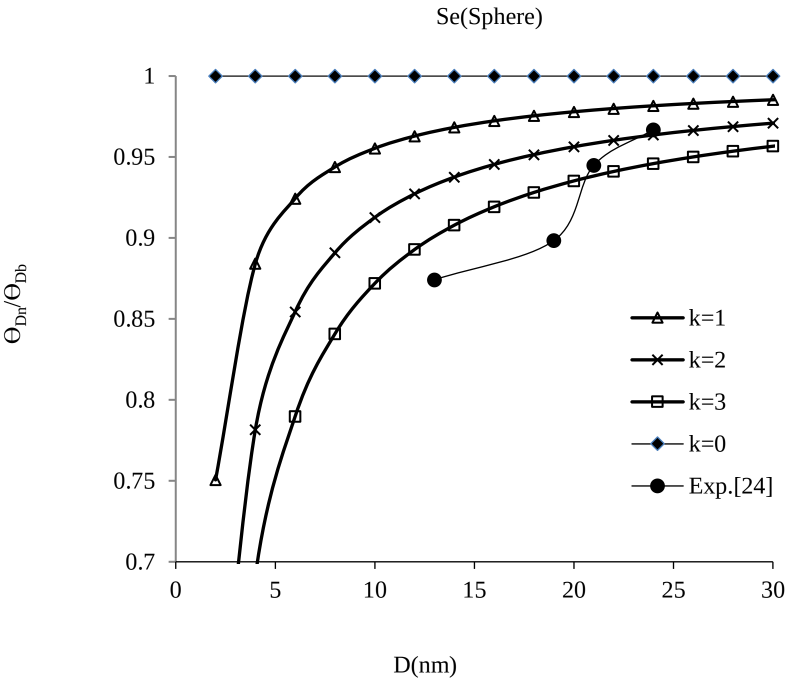

Figure1. Relative Debye temperature vs. diameter (nm) for Se nanoparticle.

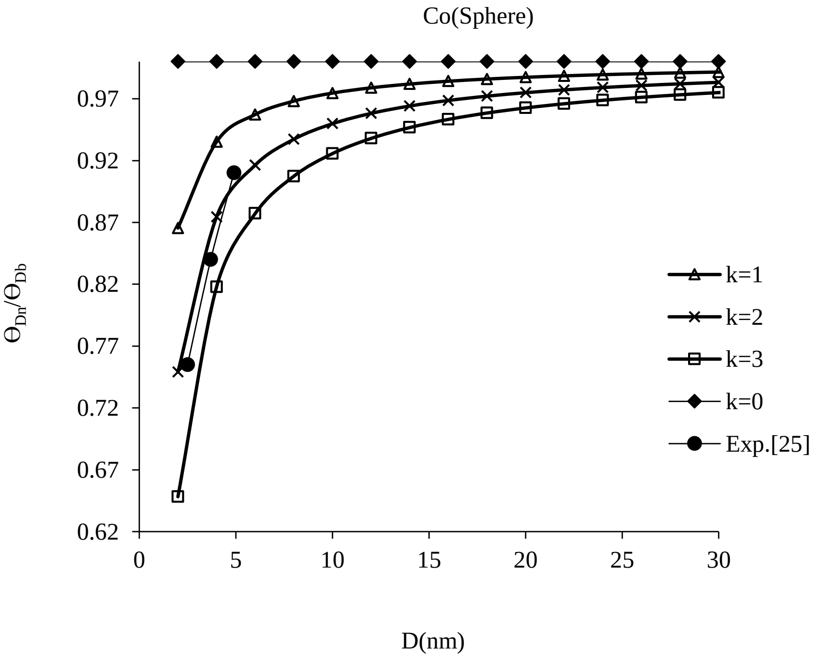

Figure 2. Relative Debye temperature vs. diameter (nm) for Co nanoparticle.

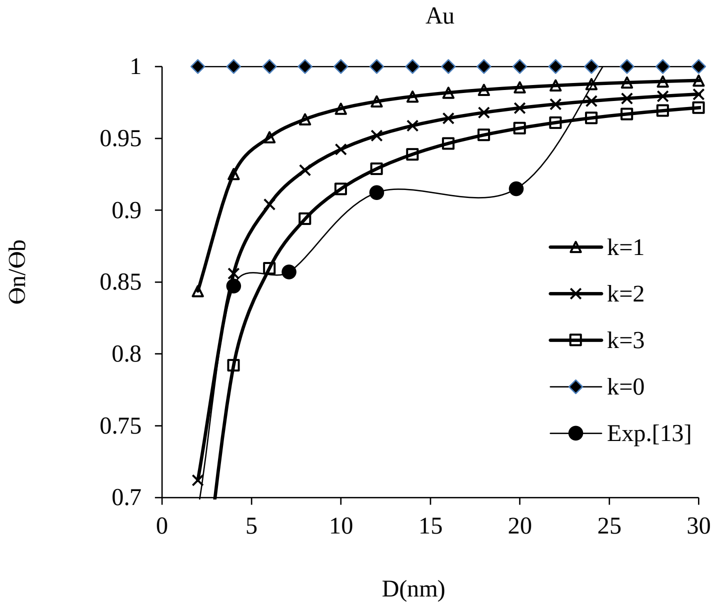

Figure 3. Relative Debye temperature vs. diameter (nm) of Au nanoparticle.

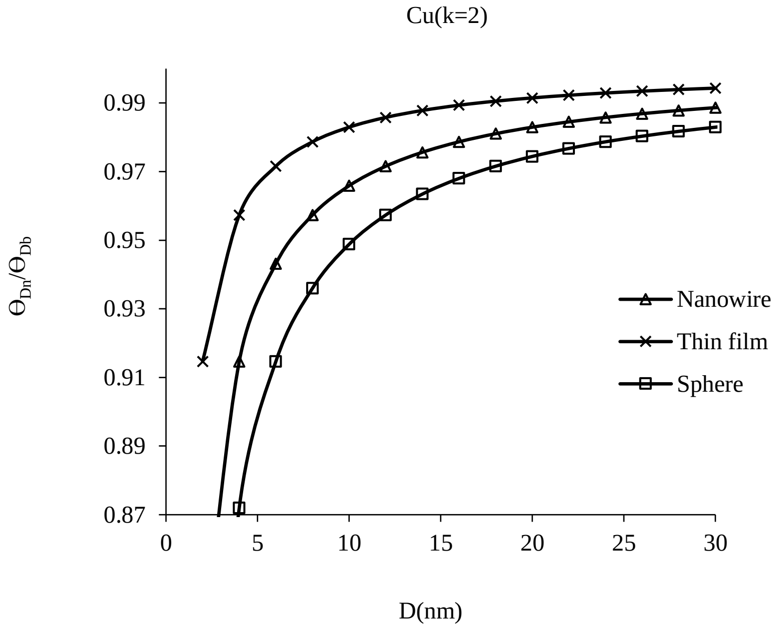

Figure 4. Relative Debye temperature vs. diameter (nm) for Cu nanomaterial.

Figure 5 is showing the effect of size on Relative Einstein temperature by considering different values of k for Se nanoparticle and the experimental results provided by Zhao et al. [24] is depicted in respective figure to check the model consistency with experimental data. Three types of nanostructures based on dimensions, i.e. spherical, thin film and nanowire are taken in Figure 6. Figure 6 depicts the dimension and size effect on Einstein temperature. The experimental data for all dimensional nanostructures is not available in the literature. It is found that the Einstein temperature is reduced as the size of nanosolid is reduced and at small size i.e. around 10 nm there is sudden fall in Einstein temperature. The variance is more for thin film shape as compared to nanowire and thin film shape. These variations are because of large surface to volume ratio in nanostructures with their size reduction to nanoscale that decreases the exchange interaction energy and inter spin interaction. This theoretical study is useful for the scientists who are doing well in research work.

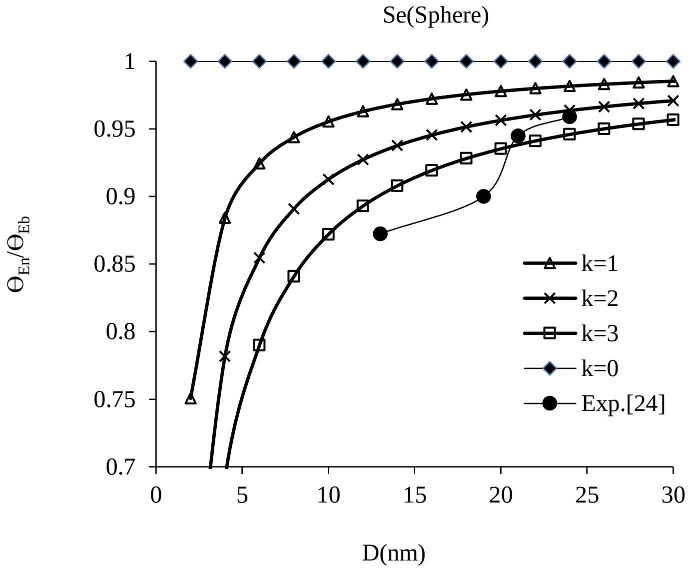

Figure 5. Relative Einstein temperature vs. diameter (nm) for Se nanoparticle.

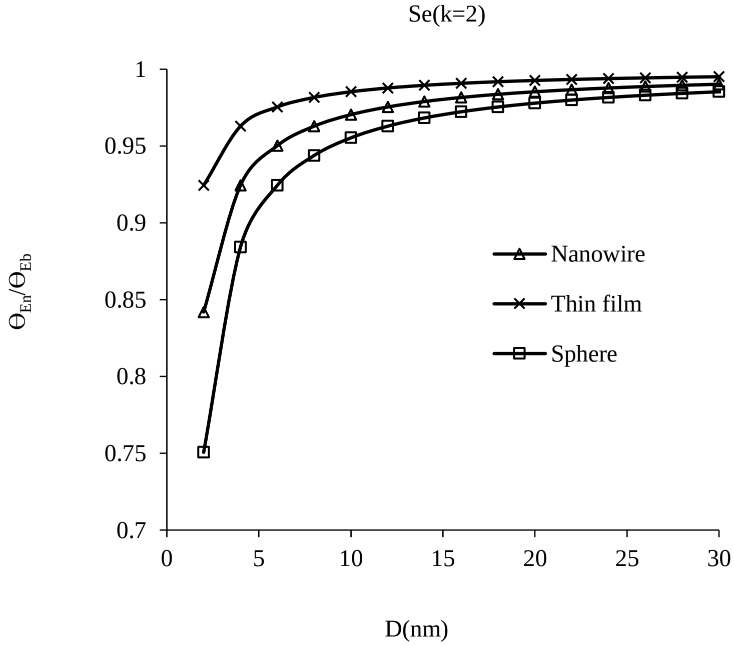

Figure 6. Relative Einstein temperature vs. diameter (nm) for Se nanomaterial.

CONCLUSION

The size dependence of Debye temperature and Einstein temperature functions are modelled for sphere, thin film, and nanowire shapes by using Bond energy model. It is found that both the parameters Debye temperature and Einstein temperature are depressed with decreasing the size of nanomaterials. A good consistency of our predictions with the available experimental results proves the superiority of this theoretical study.

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