Effect of size on Debye temperature, melting entropy and enthalpy of nanomaterials

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ABSTRACT

Size decreases ⟶ Surface area increases ⟶ Surface Energy increases

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Thermodynamic Property Changes

The energy associated with the free surface atoms will be different from the atoms of the bulk. The excess energy associated with the surface atom is called the free surface energy. In bulk materials, such free energy is neglected because it is associated with only few layers of atoms near the surface and the ratio of the volume occupied by the surface atoms and the total volume of the material is extremely small. However for the nanomaterials, the surface to volume ratio is significant. We report a theoretical model, free of adjustable parameters, the shape and size dependent Debye temperature, Melting entropy and Enthalpy of Au, Ag and In nanomaterials. We adopt the top down approach using classical thermodynamics by considering Lindemann's criterion to study the size and shape effect. The results obtained are compared with the available experimental data.

Keywords: Surface energy, cohesive energy, nanomaterials, Debye temperature, melting entropy

INTRODUCTION

Nanotechnology and nanoscience began in the early 1980's with the advances in computing power and material modelling. The term nanotechnology was originally defined by Norio Taniguchi in 1974 as follows: "nanotechnology mainly consists of the processing of separation, consolidation and deformation of materials by one atom or by one molecule." Nanomaterials are basically the link between nanoscience and nanotechnology. Over the past decade, nanomaterials have been the subject of vast interest. When the particle size of materials becomes nanoscale, optic, electronic, magnetic, catalytic, biomedical and thermodynamic properties vary noticeably from those of an isolated atom and bulk materials.[1-6] It is recognized that the size dependence of thermal stability in nanomaterials is increasingly becoming one of the major concerns in upcoming technologies.[7-8] Cohesive energy, 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.[9-11] Many experimental and theoretical efforts have been implemented to investigate the size-dependent cohesive energy of nanomaterials.[12-15] At nanoscale Ag and Au have demonstrated many interesting chemical and physical properties that their bulk counterparts do not have.[16-19]

In this paper, we derive a theoretical model for studying the particle size and shape (nanoparticles, nanowires, and nanofilms) dependent Debye temperature, melting entropy and enthalpy of Au, Ag and In naomaterials. The decreased Debye temperature, melting entropy and enthalpy of nanomaterials are explained through the effect of surface to volume ratio over the bulk materials. The study based on surface effect at decreased particle size, permits interpolation and extrapolation to the region for which adequate experimental data do not exist.

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THEORETICAL FORMULATION

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.[20] 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 written as[21]

$$\theta_b^{\,2} \propto \left(\frac{T_b}{MV^{2/3}}\right) \tag{1}$$

Equally for nanomaterial

$$\theta_n^{\,2} \propto \left(\frac{T_n}{MV^{2/3}}\right) \tag{2}$$

Where, M is the molecular mass.
Eq. (1) and Eq. (2) give the following relation

$$\left(\frac{\theta_n^2}{\theta_b^2}\right) = \frac{T_n}{T_b} \tag{3}$$

Qi[22] reported the relation based on the effect of surface to volume ratio for melting temperature of nanomaterials and bulk materials with the following relation:

$$\frac{T_n}{T_b} = \left(1 - \frac{N}{2n}\right) \tag{4}$$

From Eqs. (3) and (4), we get

$$\left(\frac{\theta_n}{\theta_b}\right) = \left(1 - \frac{N}{2n}\right)^{1/2} \tag{5}$$

On the similar ground we derived the relation for melting entropy and melting enthalpy for nanomaterials.
For melting entropy:

$$S_n = S_b + \frac{3R}{2}\ln\left(1 - \frac{N}{2n}\right) \tag{6}$$

We have the relation

$$H_n = T_n S_n$$

So, using this relation, melting enthalpy:

$$H_n = \left(H_b + \frac{3RT_b}{2}\ln(1 - \frac{N}{2n})\right)\left(1 - \frac{N}{2n}\right) \tag{7}$$

Where, N is the total number of surface atoms, n is the total number of nanosolids and R is the gas constant. 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.[22] The value of $\frac{N}{n}$ is $\frac{4d}{D}, \frac{8d}{3l}$ and $\frac{4d}{3h}$ for spherical nanosolids, nanowires and nanofilms respectively[22]. Where, d is the diameter of an atom and D is the diameter of the spherical nanosolids. l and h are the diameter of nanowire and height of the nanofilm respectively.

Melting entropy and enthalpy of metallic nanoparticles are derived by Shandiz et al.[25] which recites as

$$S_{mn} = S_{mb} + \frac{3R}{2}\ln(1 - 2(1-q)\frac{D_0}{D + D_0})$$

And

$$H_{mn}/H_{mb} = (1 - 2(1-q)\frac{D_0}{D + D_0})(1 + \frac{3R}{2S_{mb}}\ln(1 - 2(1-q)\frac{D_0}{D + D_0})$$

Where, R is the gas constant and D_0 denotes the smallest size. They assumed the value of q=1/4. But, our model is free from any adjustable parameter. This is the lead of our model with the Shandiz et al.[25]

Table 1: Input parameters[23,24]

Nmat.	d(nm)	S_b(J/mole/K)	H_b(kJ/mole)	Θ_b(K)
Au	0.228	9.34	12.5	184.5
Ag	0.319	9.16	11.30	-
In	0.329	7.65	3.29	-

RESULTS AND DISCUSSION

Input parameters[23,24] used in the calculation in Eq. (5) to Eq. (7) are listed in table 1. It is derived theoretically that the Debye temperature and the melting entropy and enthalpy depends upon the particle size. We derived Eq. (5), Eq. (6) and Eq. (7) to analysis the size dependent Debye temperature, melting entropy and enthalpy of Au, Ag and In nanomaterials in different shapes. Debye temperatures of Au and Ag nanomaterials are computed using Eq. (5) and are plotted(figure 1) along with available experimental data.[27] It is observed that Debye temperature of all these nanomaterials decreases with decrease in size. For the comparison purpose we have plotted the nanosphere, nanowire and nanofilm on the same figure for Ag nanomaterial. It is observed that the effect of size decreases we go from spherical to nanowire to nanofilm. For Au nanoparticle, our findings are slightly higher than that reported by Kastle et al.[27] up to the particle size 18nm, and the difference become smaller when the particle size is further increased. For Ag nanoparticle, the results follow a similar trend of variation as reported for Au nanoparticle. The experimental data for the Ag nanomaterial are not available in literature.
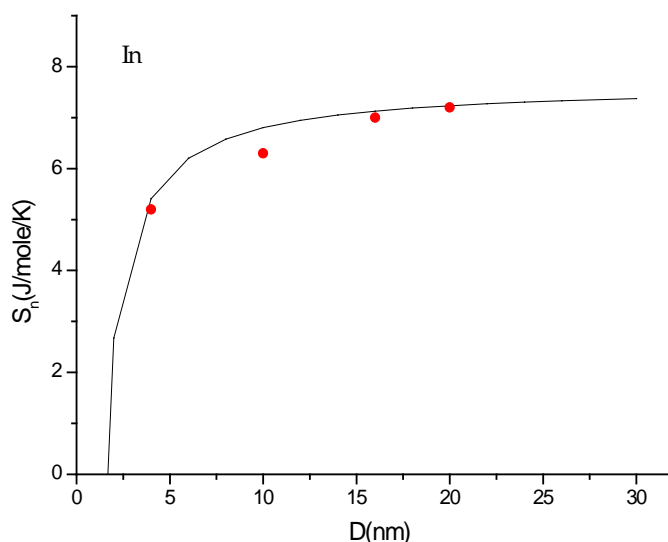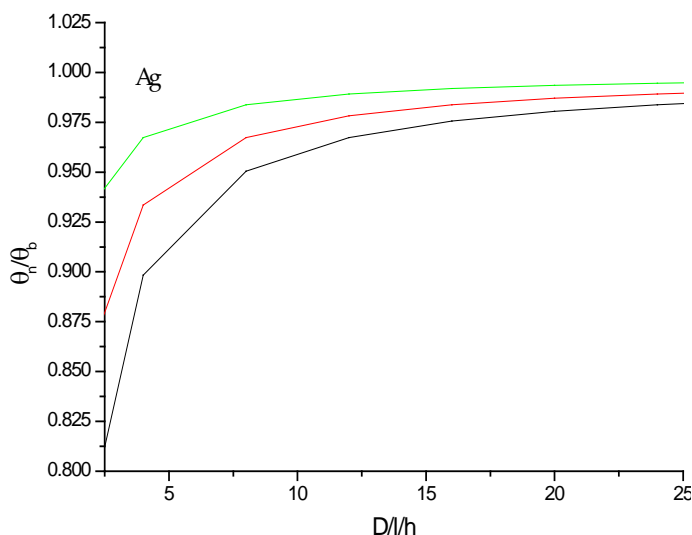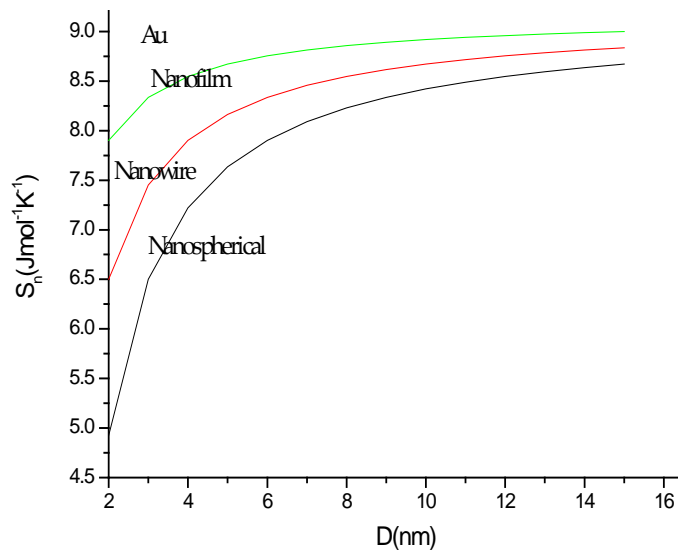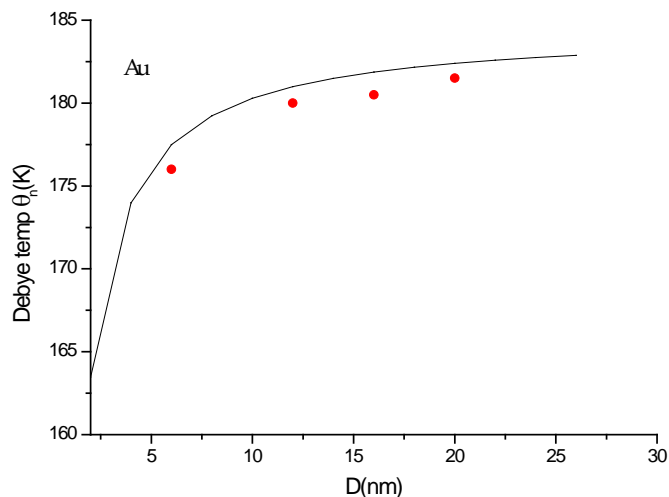
Figure 1. Size and shape dependence of Debye temperature for Au and Ag (nanosphere, nanowire and nanofilm) obtained from Eq. (5). In first figure our calculated results are shown by solid line and experimental data[27] by solid circles. In the second figure our calculate results are shown by solid lines from bottom to top for nanosphere, nanowire and nanofilm respectively

Figure 2. Size and shape dependence of melting entropy for Au and In nanomaterials obtained from Eq. (6). In the first figure our calculated results are shown by solid lines from bottom to top for nanosphere, nanowire and nanofilm respectively. In second figure our calculated results are shown by solid line for nanospherical shape and solid circles are the experimental data.[26]

The melting entropy variations of Au and In calculated by Eq. (6) are reported (figure 2). It is found that melting entropy decreases with decrease in grain size. As discussed, the melting entropy goes down with the decrease of the particle size. For the sake of comparison of In (spherical nanosolid), the experimental values[26] are shown in the figure 2 by solid dots, which support well to our calculated results. The melting entropy of In nanomaterial increases on increasing the particle size up to 15nm and is almost constant above 30nm. Our results for In nanomaterial are almost same as that reported by Safaei *et al*.[26] except around 10nm which is slightly above the experimental value. There is a good agreement between theory and the experimental value above 18nm. It is found that the melting entropy of In nanomaterial increases up to 30nm.This added the validity of the model exercised. The experimental values for the size dependence melting entropy of Au nanosolids do not exist in the text. Although, the trend of variations are similar to that

obtained for melting entropy of In. Also, we have studied the size and shape dependent melting enthalpy of Ag and In nanomaterials. The results obtained by using Eq. (7) are reported (figure 3). The melting enthalpy of Ag nanomaterial increases with increase in particle size up to 20nm and more or less persistent above it. Our findings are slightly higher than that conveyed by Safaei *et al*.[26] The melting enthalpy for In nanomaterial is shown (figure 3). For In nanomaterial the results revealed by the Eq. (7) are slightly lower that of discussed by Safaei *et al*.[26] up to the 30nm particle size. When the particle size is less than 15nm, there is a sharp decrease the value of melting enthalpy with decreasing particle size. Above 15nm, there is slightly increase the value of enthalpy with particle size. It may be concluded that the melting enthalpy of the nanomaterial decreases as the particle size decreases for all the cases considered in the present study. There is a good accord between the calculated

results and the available experimental data[26] for spherical shape. It is found that the enthalpy decreases with decrease in particle size. Definitely, by decreasing particle size, more and more portion of atoms occupy surface sites, which are able to move freely more than the interior atoms of nanomaterials. Consequently, Debye temperature, entropy and enthalpy of melting decrease with decrease in particle size.

On decreasing size, the surface to volume ratio increases, which increases the surface energy. Since Debye temperature, entropy and enthalpy of melting depends upon the value of N/2n. The increasing value of N/2n which is 2d/D for nanoparticle, 4d/3l for nanowire and 2d/3h for nanofilm increases with decreasing the particle size. Therefore, the increase of 2d/D, 4d/3l and 2d/3h decreases the Debye temperature, entropy and enthalpy of melting of the nanomaterials.
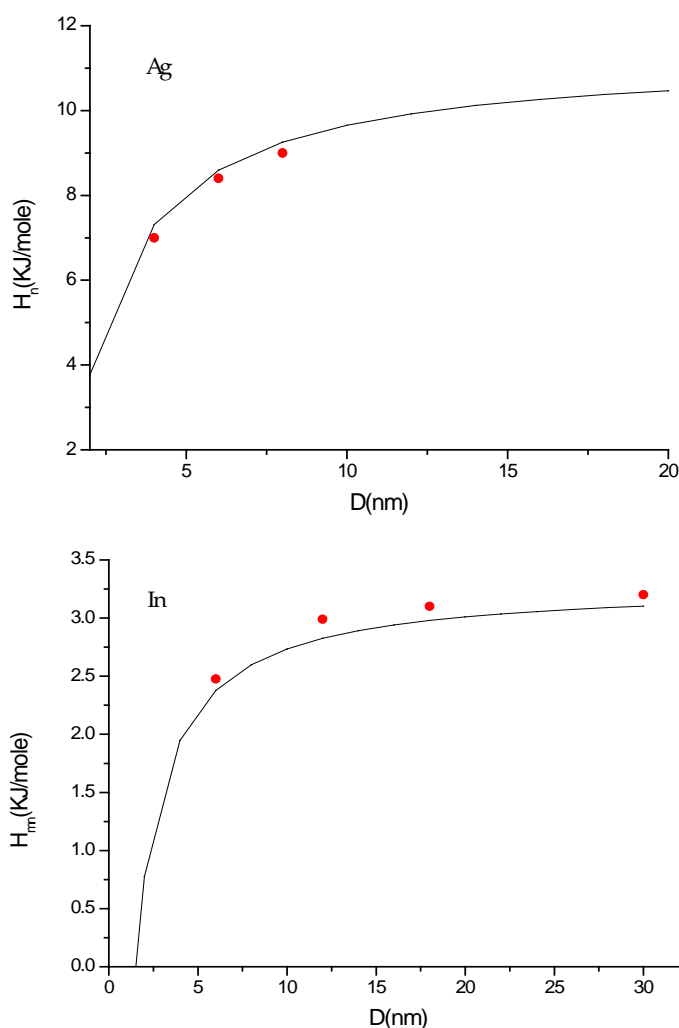

Figure 3. Size and shape dependence of melting enthalpy for Ag and In nanomaterials obtained from Eq. (7). Our calculated results are shown by solid lines for nanospherical shape and solid circles are the experimental data.[26]

CONCLUSIONS

Size dependence Debye temperature, melting enthalpy and entropy of nanomaterials in different shapes (nanosphere, nanowire and nanofilm) have been studied. It is shown that the calculated results of Debye temperature, melting entropy and

enthalpy of Au, Ag and In nanomaterials are consistent with the available experimental results. Also, it is found that the particle shape effect the Debye temperature, melting entropy and enthalpy of the nanomaterials. The effect becomes more with the reducing of particle size. The method presented in this paper might have potential application to find the size dependent thermodynamic properties of nanomaterials.

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