Thermodynamic study of nanometals for different shapes and sizes

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Thermodynamic analytic model has been discussed to study the size as well as shape effect on thermodynamic parameters of nanometals. Thermodynamic properties like melting temperature, cohesive energy, vacancy formation energy and Debye temperature of Al, Ag, Au, In and Sn nano metals for spherical and non spherical nanoparticles (i.e. tetrahedral, hexahedral, octahedral and disc like) with different size have been studied. Present study shows that spherical and nonspherical nanoparticles behave in different manner due to the difference in their shape factor. It has been found that these thermal properties show decreasing trend with decrement in size of the nanomaterial due to the change in surface to volume ratio. The obtained results also reveal that shape of the nanoparticle plays a vital role to affect the thermodynamic properties of small sized nanoparticles because of change in surface area with shape for fixed volume. Theoretical results obtained for melting temperature, cohesive energy, vacancy formation energy and Debye temperature have been discussed in the light of available simulated and experimental data which supports the validity of present model.

Keywords: Cohesive energy, Melting, Nanoparticles, Thermal properties

1 Introduction

Materials with reduced size such as nanowires, nanotubes, nanofilms and nano particles depict different properties from those of the bulk materials[1]. Nowadays nanomaterials have become one of the most vigorous fields of research because at this scale a unique optical, thermodynamic, magnetic, electrical and other property emerges[2,3]. A detailed study of the thermal properties of nanomaterial is of importance because of their various applications in the different field of science and engineering[4,5]. Total number of atoms in any nanomaterial is the sum of surface and interior atoms. As the size of the materials shrinks the total number of atoms in it also becomes less and the surface to volume ratio increases. Due to the limited number of atoms and increased surface to volume ratio at nano range, the shape becomes an important factor which should not be ignored because of the change in surface area for fixed volume. In the past few years polyhedral nanoparticles have also been observed and these nanoparticles are of great use due to their structure like non spherical gold nanoparticles have fantastic optical features due to the presence of multiple absorption bands correlated with their axes[6,8]. It is possible to produce nanoparticles of different shapes since now the controlled synthesis of nanoparticles is not restricted up to the size but can

also be control the shape of the nanoparticle[9-11]. These facts show that while studying the thermodynamic properties of a nanomaterial the shape is a substantial factor.

A bulk material has specific value of melting temperature, cohesive energy, surface energy, Debye temperature etc., this is due to the well defined arrangement of atoms. While for nanomaterials arrangement of atom, number of surface atom and bonding between atoms changes and edge effect comes into play and as a result these properties vary with shape and size. Melting of a material is a very common and one of the important phase transformations. From past few years theoretical and experimental studies are going on simultaneously with computer simulations. In some experiments, it has been reported that some nanoparticles have higher value of melting temperature compared with bulk sized material known as superheating, while some other nanoparticles have opposite behavior. Super heating is expected, when nanoparticle with lower surface energy are embedded in a matrix of material having higher surface energy[12,13]. There are various models have been developed to understand the size dependent physical properties of nonmaterial till now[14,18]. A widely used thermodynamic model of Qi and Wang assumed that the cohesive energy of a nanomaterial is the sum of energies of interior and surface atom with the concept of dangling bond at the

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surface[19]. Thermodynamical properties like cohesive energy, melting temperature, Debye temperature etc has been discussed for different size with the help of this model.

In the present work the model consisting shape effect incorporated with size has been applied for analyzing thermal properties (i.e., cohesive energy, melting temperature, Debye temperature and vacancy formation energy) with spherical, tetrahedral, octahedral, hexahedral and disc like shape particles for Al, Ag, Au, In and Sn nano metals. As the size of particle decreases, they have unique atomic structure, which is quite different from their bulk counterpart. Moreover due to a limited number of atoms in nanorange the shape becomes an important factor. Since, the surface area changes with the shape of nanoparticles, which affects the surface to volume ratio of atoms. Melting is initiated from the surface which is a consequence of poor stability of the surface. since, the amplitude of the thermal vibrations of the surface atoms is larger than the bulk ones. Once the melting temperature is known the other parameters like cohesive energy, Debye temperature etc. can be determined from it, using thermodynamic relations.

This work is also continued very first time for analyzing both the shape and size effect on the vacancy formation energy of nanometals. Tiwari and Patil[20] described the two approaches to find the relation between cohesive energy and vacancy formation energy. If an atom is missing from its lattice site then a vacancy is created. Vacancy formation energy is the energy required to break the interatomic bonds around one atom.

2 Models

2.1 Melting temperature and cohesive energy

The shape of the nanoparticles can be categorized in spherical and non spherical shape. According to the definition of shape factor $\alpha = s'/s$, where $s' =$ surface area of non spherical nanoparticles, $s =$ surface area of spherical nanoparticle[21]. It should be noted that the nonspherical and spherical nanoparticles would be of the same volume. For the spherical nanoparticles, the shape effect can be ignored due to the unit value of shape factor .While for non spherical shapes; shape effect should be included due to having the value of shape factor greater than one[22]. Qi and Wang model is the simplest and a reliable model for studying the thermodynamic parameters like melting point,

cohesive energy etc of nanomaterials. Cohesive energy is the energy required to break all bonds associated with one of its constituent's molecules. In other terms cohesive energy is the measurement of strength of the bonds.

According to the above definition of cohesive energy Qi and Wang proposed a model assuming that cohesive energy E of nanomaterials is the sum of bond energies of surface and interior atoms[19]:

$$E(d, \alpha) = \frac{1}{2}\left[\frac{\beta}{4}\left(4\alpha\frac{R^2}{r^2}\right) + \beta\left(\frac{R^3}{r^3} - 4\alpha\frac{R^2}{r^2}\right)\right]E_{bond} \quad \text{... (1)}$$

where, E_{bond} is bond energy and β is the number of bonds. Here r is the atomic radius ($2r = d$) and R is the radius of nanoparticle. First term corresponds to the surface atom and is multiplied by $\frac{\beta}{4}$ factor, which is the number of surface bonds. As, the atoms on surface possess few nearest neighbors or coordination number so it has dangling or unsatisfied bonds. Reducing the Eq. (1) in the form of:

$$E(d, \alpha) = E_O\left(1 - 3\alpha\frac{d}{D}\right) \quad \text{... (2)}$$

Here $E_O = \frac{1}{2}n\beta E_{bond}$ is the cohesive energy of bulk materials.

According to Rose et al.[23-25] model, the cohesive energy of the solids and the melting temperature are linearly related hence melting temperature of nanomaterial (T) should follow a relation similar to Eq. (2):

$$T(d, \alpha) = T_O\left(1 - 3\alpha\frac{d}{D}\right) \quad \text{... (3)}$$

Here T_O, be the melting temperature of corresponding bulk material, d is the atomic diameter and D is the size of nanoparticle. Equation (3) can be used for determining the melting temperature of nano particle with any shape and size.

After putting the calculated values of shape factor[22] α in Eq. (3) from Table 1, we get the size and shape dependent equations for melting temperature. Cohesive energy of different shapes follows the same equations due to linear relationship with melting temperature.

Table 1 – Shape factors for different shapes of nanoparticles

Particle shape	Shape factor[22] (α)
Spherical	1
Regular tetrahedral	1.49
Regular hexahedral	1.24
Regular octahedral	1.18
Disc	3.09

2.2 Debye temperature

Lindemann proposed a simple model of melting, which states that a solid can liquefy when the root-mean-square average amplitude σ of the atomic thermal vibrations reaches a certain fraction of the nearest interatomic spacing[26] h. This model relates the melting temperature with the Debye temperature by the relation[27] (M is the molar mass and V is the molar volume):

$$\theta_{D0} = c \left[\frac{T_0}{M V_s^{2/3}} \right]^{\frac{1}{2}} \qquad \ldots (4)$$

This Eq. (4) also holds for nanomaterials and can be written as follows:

$$\frac{\theta_{Dn}}{\theta_{D0}} = c \left[\frac{T}{T_0} \right]^{\frac{1}{2}} \qquad \ldots (5)$$

With the help of Eqs (3) and (5):

$$\frac{\theta_{Dn}}{\theta_{D0}} = \left[1 - \frac{3\alpha d}{D} \right]^{\frac{1}{2}} \qquad \ldots (6)$$

After putting the values of shape factor α in Eq. (6), we get five equations of Debye temperature for spherical and non spherical shapes.

2.3 Vacancy formation energy

Another important property at the nanolevel is vacancy; it is nothing but a point defect in a crystal. As the size of the material reduces, the vacancies may be form due to the rearrangement of atoms and their deformation. The Vacancy formation energy is the energy required for breaking the bond between the atom and its neighbour atom and it has been discussed by Qi and Wang[28]. As the shape of nanoparticle changes, arrangement and the bonding between the atoms will be change, so it is necessary to include the shape effect on vacancy formation energy.

As the bonds breaks vacancy is formed, due to this the change in surface energy takes place. When the spherical particle is taken out from an ideal crystal, Surface energy can be written as, $S = 4\pi R^2 \gamma$. If the shape of the nano particle is non spherical, shape effect is considered then surface energy is $S' = \alpha 4\pi R^2 \gamma$ (R is the radius of nanoparticle and γ is surface energy per unit area at temperature T).

When a nanoparticle is taken out then due to the surface tension some contraction takes place in nanoparticle size and let this contraction in any nanoparticle be equals to εR (R is the radius of ideal nanocrystal), ε is a very small quantity. Due to this contraction the surface energy will be increased by[29]:

$$\Delta S = \alpha . 4\pi [R(1-\varepsilon)]^2 \gamma \qquad \ldots (7)$$

Increased elastic energy of spherical nano material is $\pi^{-\frac{1}{2}} S^{\frac{3}{2}} G \varepsilon^2$ (G is the shear module) and for non spherical shape surface energy is $\alpha^{\frac{3}{2}} \pi^{-\frac{1}{2}} S^{\frac{3}{2}} G \varepsilon^2$.

The total energy change is:

$$\alpha . 4\pi [R(1-\varepsilon)]^2 \gamma + \alpha^{\frac{3}{2}} \pi^{-\frac{1}{2}} S^{\frac{3}{2}} G \varepsilon^2 \qquad \ldots (8)$$

In equilibrium, the total energy variation is found minimum:

$$\varepsilon = \frac{1}{1 + \left(\frac{2G}{\gamma}\right) R \, \alpha^{\frac{1}{2}}} \qquad \ldots (9)$$

Due to the contraction the resultant atomic radius (r_p) becomes, $r_p = r_o (1 - \varepsilon) = r_o \left(\frac{KD}{KD+1}\right)$ and $K = \alpha^{\frac{1}{2}} G/\gamma$. The vacancy formation energy of a nanoparticle with r_p radius is given by:

$$E_P = 4\pi r_p^2 \gamma_o \left[\frac{1}{1 + \gamma_o/(2Gr_p)} \right] \qquad \ldots (10)$$

After putting the value of r_p in terms of r_o, we get the final shape dependent expression for vacancy formation energy:

$$E_P = E_O \left(1 + \frac{\beta}{D} \right)^{-1} \qquad \ldots (11)$$

where $\beta = \frac{4Kr_o + 3}{2K^2 r_0 + K}$, E_O is the vacancy formation energy of the bulk and K is shape dependent parameter.

3 Results and Discussion

The size and shape dependent thermodynamic properties of Al, Ag, Au, In and Sn nanometals for five different shapes, i.e., spherical, regular tetrahedral, regular octahedral, regular hexahedral and disc like shape have been studied. The value of shape factor for the non spherical nanoparticles varies with shape while for spherical shape it is equal to one. In the case of disc shaped nano particle shape factor is given by α = (1+x)/ (1.65∗x $^{(1/3)}$), where radius (l) =x (constant)∗ height (h). It was assumed here that the radius (l) is ten times greater than the height (h) of particle, and the shape factor come out as 3.09. Hence, the shape factor can be varied according to the relationship between radius and height. The Melting temperature and cohesive energy of these nanometals have been calculated for different shapes using Eq.

(3). The obtained theoretical results of these properties are graphically represented and compared with the available experimental and simulated data of spherical nanoparticles only due to the unavailability of experimental data for nonspherical shapes. The Input parameters needed are tabulated in Table 2.

Figure 1(a-e) shows melting variation of Al, Ag, Au, Sn and In respectively with size for different

Table 2 – Input parameters used in calculation

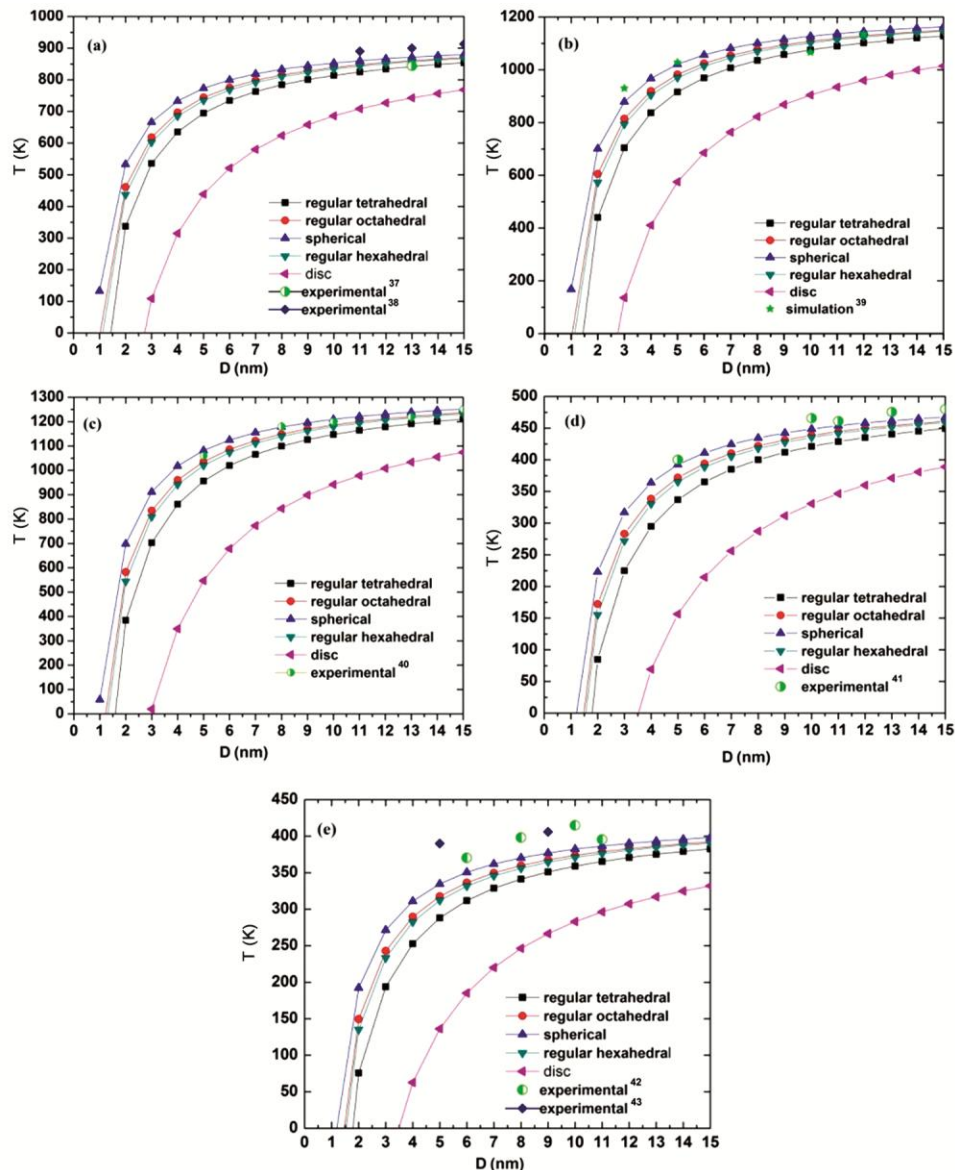| Nanomaterials	T_0 (K) (Ref.[31])	E_o (KJ/mol) (Ref.[30])	Θ_D (K) (Ref.[32])	Atomic diameter d (nm)	Surface energy at 298 K (J/m^2) (Ref.[33])	Shear module at 298 K$\times 10^{10}$ (N/m^2) (Ref.[34])
Au	1337.6	368	170	0.3188 (Ref.[35])	1.508	2.60
Ag	1234.0	284	215	0.2880 (Ref.[31])	1.250	3.03
Al	933.25	327	428	0.2460 (Ref.[36])	1.146	2.62
Sn	505.10	303	140	0.3724 (Ref.[36])	0.709	0.368
In	429.80	243	108	0.3685 (Ref.[36])	0.700	1.84

Fig. 1 – Size and shape dependent melting temperature for (a) Al, (b) Ag, (c) Au, (d) Sn and (e) In nanoparticles with different shapes

shapes along with the available experimental and simulated results[29-33]. All these nanometals show decreasing trend of melting temperature with decrement of size due to increase in the number of surface atoms same as shown by experimental and simulated data, which supports the validity of these shape and size dependent equations. It can also be seen that shape effects are more prominent for small range nano particles.

It can be observed from graphs that melting temperature is maximum for spherical shape and minimum for disc like shape because sphere has minimum surface area and disc have maximum surface area among the considered shapes; hence the numbers of surface atoms are less with respect to interior volume in spherical shape, which gives the higher value of melting temperature. As the size of nanoparticle increases, number of interior atoms increases which suppresses the shape effect. Error bar diagrams from Fig. 2 also explain the deviation of

calculated theoretical values for melting temperature of spherical nanoparticles from the experimental data.

Variation of cohesive energy for different shapes with size has been plotted in Fig. 3(a-e) for Al, Ag,
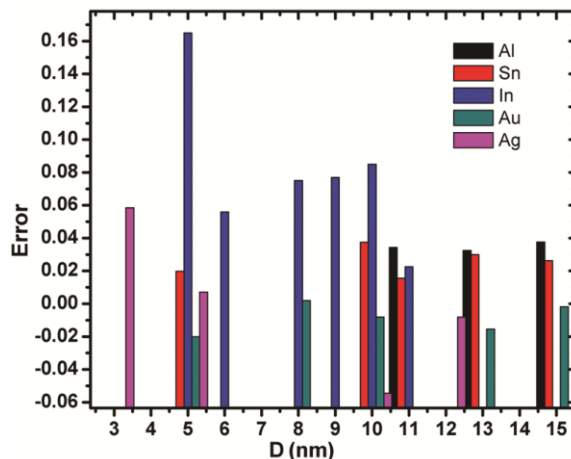

Fig. 2 – Deviation in calculated values from experimental values of melting temperature for Spherical nanoparticles at various sizes
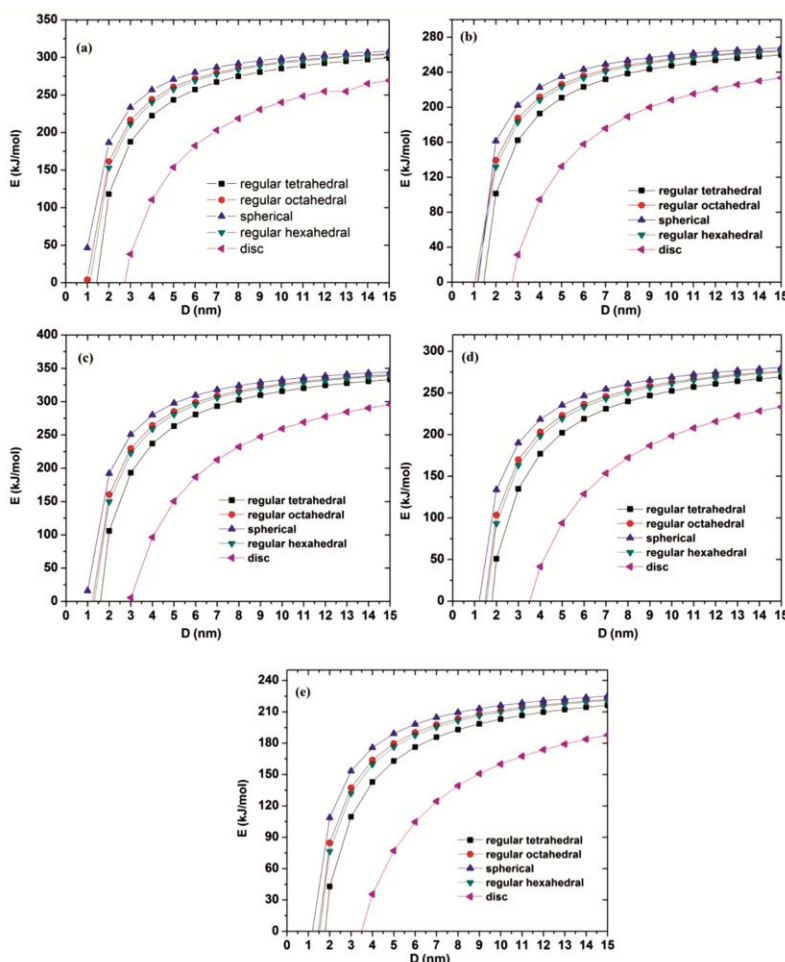

Fig. 3 – Size and shape dependent cohesive energy for (a) Al, (b) Ag, (c) Au, (d) Sn and (e) In nanoparticles with different shapes

Au, In and Sn nanometals, respectively. Obtained results for cohesive energy also show the similar decreasing trend with decrement of size as shown by melting temperature due to linear dependency. For small nano particles most of the atoms are at surface, so their bonding becomes weak with interior atoms that can be break easily by giving small amount of energy. While in bulk materials, most of the atoms are in the interior so it is not possible to break the bond by such a little amount of energy, hence cohesive energy reduces with size reduction. Cohesive energy varies with the shape of the nanoparticle; from graphs it was found that for spherical shape it has maximum value and minimum for disc like

shape. For spherical shape nanoparticles, the interior bonding is significant but numbers of surface atoms are less so they possess dangling bonds at the surface. While in disc shape nanoparticles surface is highly reactive among the considered shapes.

Variation of Debye temperature for five nanoparticles has also been calculated theoretically in the light of Eq. (6). Graphical representations of calculated results are shown with available experimental data[34] in Fig. 4(a-e) for Al, Ag, Au, Sn and In nanometals, respectively. Error bar diagram for gold (Au) nanoparticle is shown in Fig. 5. All input parameters are tabulated in Table 2. It can be
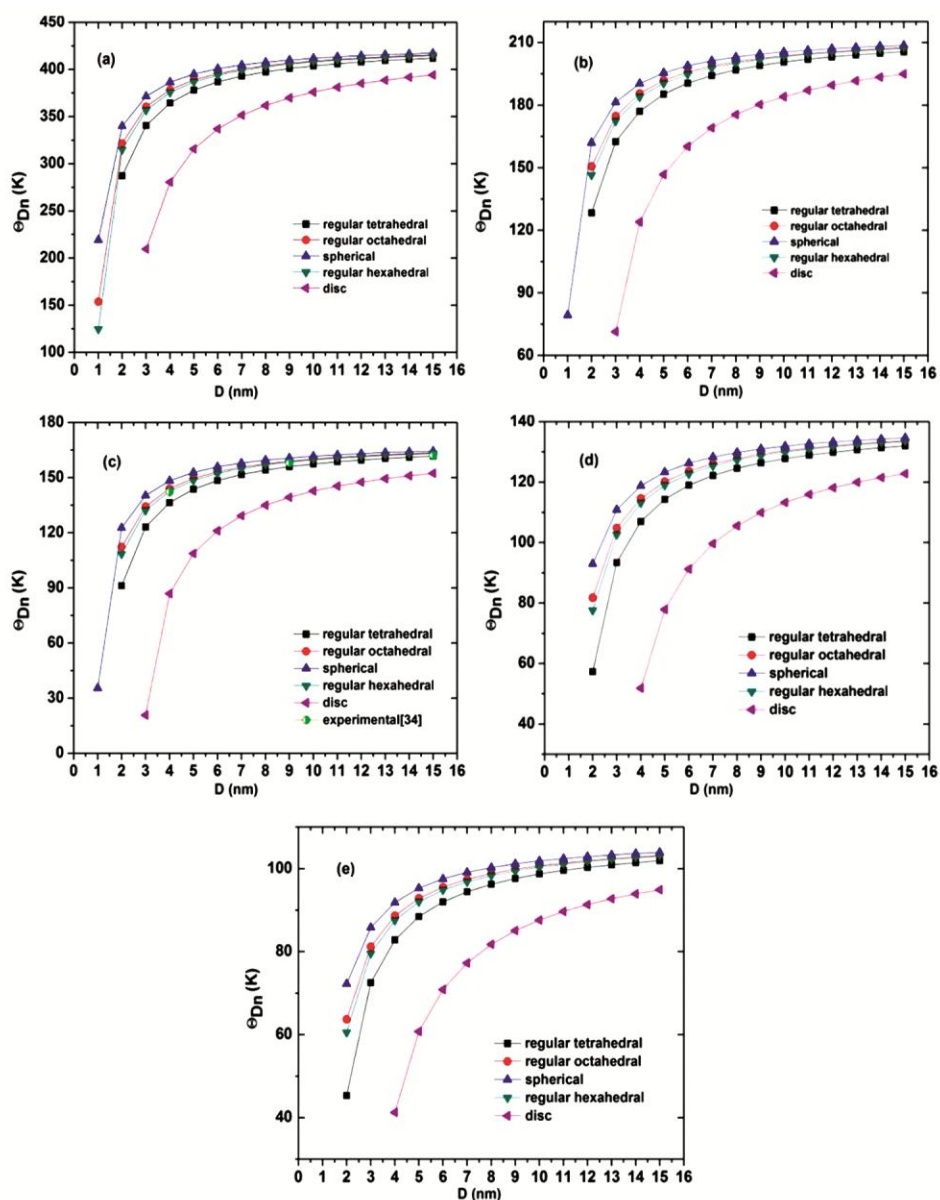

Fig. 4 – Size and shape dependent Debye temperature for (a) Al, (b) Ag, (c) Au, (d) Sn and (e) In nanoparticles with different shapes
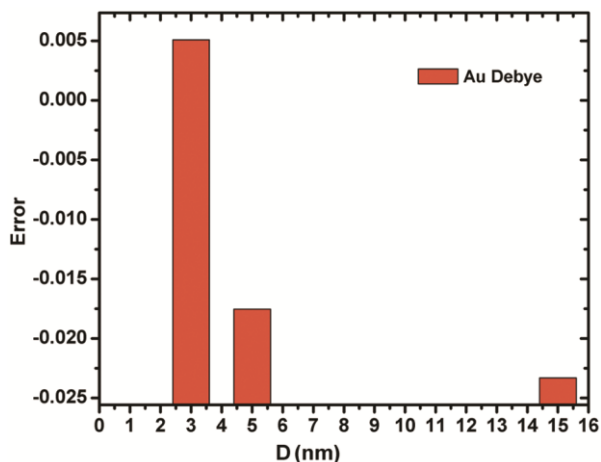
Fig. 5 – Deviation in calculated Debye temperature from experimental data for gold (Au) spherical nanoparticles at various sizes

observed from the graphs that Debye temperature θ_{Dn} shows the decreasing trend with decrement of size. It is observed Debye temperature of nano metals have maximum value for spherical shaped nanoparticles and lowest for disc shaped nanoparticles. As Debye temperature is related with the frequency of vibration, which is large for the atoms of the spherical shaped nanoparticle and least for the disc shaped nanoparticles.

For the study of vacancy formation energy Eq. (11) has been used. Plot of vacancy formation energy variation, for different shapes with size of nano Al, Au, Ag, Sn and In are shown in Fig. 6(a-e) respectively. From the graphs, we can see that vacancy formation energy also decreases as the size reduces. Only calculated results are given in the lack of experimental data. The trend of the graphs reveals
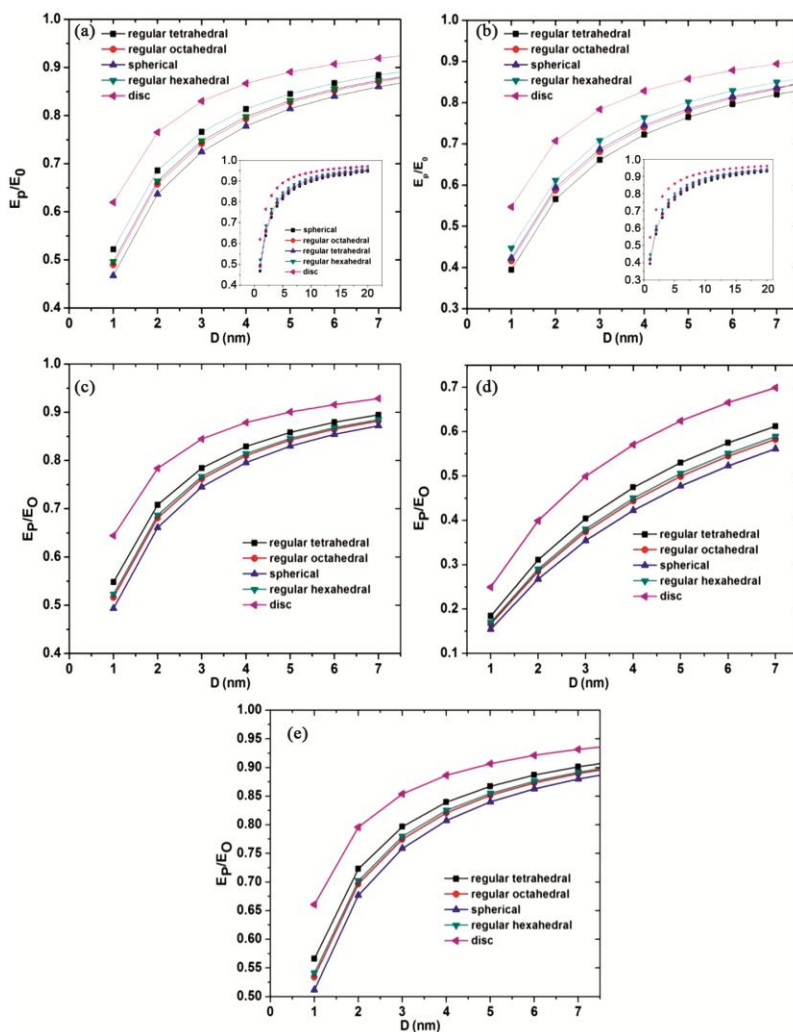

Fig. 6 – Size and shape dependent vacancy formation energy for (a) Al, (b) Au, (c) Ag, (d) Sn and (e) In nanoparticles with different shapes

that the ease of formation of vacancy increases as the size of the material reduces. As the size reduces, the surface energy of nanoparticle increases and the bonding between the surfaces atoms get weaker, which makes them more reactive than its bulk counterpart. So, it is easier to remove an atom or to create a vacancy in small sized nanoparticle. Shape effect can also be observed from the graphs that it is easy to create vacancy in spherical shape and it becomes little harder for disc like shape among all the shapes taken in to consideration. Since for spherical shape number of surface atoms is small due to smaller surface area, the bonding between the surface atoms are weakest among all the shapes so they can be easily detached from the neighboring atoms. While for the disc shaped nanoparticles, value of shape factor is 3.09. Which is largest among the considered shapes, so it is difficult to remove an atom from the surface of disc shaped nanoparticles comparative to other shapes. When the particle size is quite large (>10 nm), shape effect is negligible and approaches to the value of corresponding bulk material.

4 Conclusions

Thermodynamic qualitative model has been extended to study shape effect incorporated with size for melting temperature, cohesive energy, vacancy formation energy and Debye temperature of small nano metals. On the basis of which by introducing the shape factor, the difference between the spherical and nonspherical nanoparticles was determined. According to this investigation, it was found that these thermophysical properties decrease as the size of the material reduces due to increase in the surface to volume ratio. It has also been observed for small sized nanoparticles, thermal properties show variation with shapes due to change in surface area. It was found shape factor plays an important role for small nanoparticles, although its effect becomes negligible for corresponding bulk material. Only the qualitative effect of shape on thermophysical properties has been discussed here. However the quantum effect is prominent for very small sized nanoparticles, which has been ignored in the present study, the phononic contribution can also be incorporated in future to analyze the quantum effect along with shape and size. Experimentally polyhedral small sized nanoparticles have also been observed but thermal studies of these particles are lacking, so this both shape and size dependent model have potential application for the experimental research of temperature based phenomena of nanoparticles.

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