Modeling for the study of thermophysical properties of metallic nanoparticles

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Abstract

Successful description and explanation of thermophysical properties at the nano level is a task of great challenge even yet today. Although great effort has been made by pioneer workers and scientists in this field but still the exact model for the prediction and explanation of these properties is lagging. In the current work, we have proposed a new model to calculate the thermophysical properties like specific heat, melting enthalpy, and melting entropy of nanomaterials, which are calculated with the help of a cohesive energy model including shape effect in addition to structure of materials at the nano level. The relaxation factor due to the dangling bond at the surface of nanoparticles is taken under consideration. The obtained results using this model is fully consistent with the available experimental findings for the above said thermophysical properties for silver (Ag), copper (Cu), Palladium (Pd), Aluminium (Al), and Indium (In). This encouraging idea has also been used to predict the nature of variation of above mentioned important thermodynamic properties of other materials at their nano level.

Keywords Nanomaterial · Shape factor · Relaxation factor · Packing fraction · Thermophysical properties

1 Introduction

During the last two decades, researchers have found a new emerging field of research as “Nanoscience & Nanotechnology” which changed our thinking about the physical phenomenon at low dimensions of the materials. This new emerging field found special attention among the researchers. This field of research is very wide and interdisciplinary having demanding applications in the industries and medical sciences. The field of nanoscience and nanotechnology is very interesting and exciting due to its strong size and shape dependence of materials at the nano level. Unfortunately, it can't be described and explained successfully by normal theories used for the materials at their bulk counterparts [1–7]. The surprising behavior of materials at the range of nano-level is due to the large

surface to volume ratio and probably due to change in the structure of the material [8]. There are various models like lattice vibration-based model, the surface to volume atom ratio model have been developed to explain the unusual behavior of nanomaterials [9–11] but still, there is no suitable theoretical model which could explain and describe the unusual behavior of nanomaterials at different segment of their sizes. It is also noticed that none of the existing models can describe the thermophysical properties for all the nanomaterials at their different size range. As we know the cohesive energy is a very important thermodynamic parameter that plays an important role to predict the various thermophysical properties, viz. melting point, Debye temperature, melting enthalpy, entropy, etc.

We have investigated some important thermophysical properties like specific heat, melting enthalpy, and

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melting entropy of some nanomaterials with the help of a proposed new model. The result obtained with the help of this present model has also been compared with the available experimental results as well as with the results of other models. It is observed that the values computed with the help of our new proposed model, are in good agreement with the available experimental results. Thus, the present model can be used to predict the thermophysical properties of nanomaterials up to the desired level of their sizes.

2 Method of analysis

Most of the small-sized materials adopt the spherical shape but in some specific cases they may acquire the non-spherical shape at the nano level. Therefore, there is a need to describe the shape factor for nanoparticles before discussing the shape effect on various physical properties of nanomaterials. For the simple understanding of the shape effect of nanoparticles, let us introduce a parameter- shape factor [12] α , defined as the ratio of surface area of the non-spherical nanoparticle (S') to the surface area of spherical nanoparticle ($S = 4\pi R^2$) of the same volume. Now the surface area of nanoparticle in any shape will be

$$S' = \alpha \cdot 4\pi R^2 \quad (1)$$

where R be the radius of spherical nanoparticle.

As the atoms are assumed to be an ideal sphere, the contribution of the number of atoms at the particle surface is given by the following equation

$$N = \frac{\alpha \cdot 4\pi R^2}{\pi r^2} = 4\alpha \frac{R^2}{r^2} \quad (2)$$

where πr^2 is the surface area of individual atoms constituting the nanoparticles and ' N ' is the number of surface atoms. As the volume of the non-spherical nanoparticle V is the same as that of the spherical nanoparticle, the total number of atoms in non-spherical nanoparticles is

$$n = \frac{R^3}{r^3} \quad (3)$$

We know that the cohesive energy (E_n) of a nanoparticle having a total ' n ' number of atoms, is given by [1]

$$E_n = (n - N)E_{cb} + NE_s \quad (4)$$

where E_{cb} is cohesive energy of bulk material, E_s is cohesive energy of surface atoms and N is the number of surface atoms in the nanoparticle.

Relating the relaxation factor δ (δ lies between 0 and 1) [13] with E_s , we have

$$E_n = (n - N)E_{cb} + N(1 - \delta)E_{cb} \quad (5)$$

$$E_n = nE_{cb} \left[1 - \frac{N}{n}\delta \right]$$

Now, the cohesive energy of nanoparticle per atom (E_{cn}) is given as

$$E_{cn} = E_{cb} \left[1 - \frac{N}{n}\delta \right] \quad (6)$$

Using the value of $\frac{N}{n} = \frac{4\alpha d}{D}$ [13] in Eq. (6), we have

$$E_{cn} = E_{cb} \left[1 - \frac{4\alpha\delta d}{D} \right] \quad (7)$$

Here α is shape factor [5], d is atomic diameter and D is size of nanoparticle.

Again, including the effect of structure of nanoparticle i.e. effect of packing fraction η [14], Eq. (4) becomes

$$E_{cn} = E_{cb} \left[1 - \frac{4\alpha\delta d}{\eta D} \right] \quad (8)$$

Thus, the Eq. (7) can be applied to predict the shape and size dependent cohesive energy of nanoparticles.

Again, the well-known empirical relation between melting temperature and cohesive energy for the pure metal [15–18], is given by

$$T_{mb} = \frac{0.032}{k_b} E_{cb} \quad (9)$$

where, T_{mb} is the melting temperature of metals in its bulk state and k_b is the Boltzmann's constant. Replacing the cohesive energy of solid E_{cb} for bulk materials by more general formula for the nanomaterials E_{cn} , we can write

$$T_{mn} = \frac{0.032}{k_b} E_{cb} \left[1 - 4\alpha\delta \frac{d}{\eta D} \right] \quad (10)$$

or,

$$T_{mn} = T_{mb} \left[1 - 4\alpha\delta \frac{d}{\eta D} \right] \quad (11)$$

According to the Lindemann criterion, the melting of crystal starts when the root mean square displacement of atoms exceeds a certain interatomic distance in the crystal [19]. The Debye temperature θ_D is related to melting temperature as,

$$\theta_D = \text{constt} \left[\frac{T_m}{M V^{2/3}} \right]^{1/2} \quad (12)$$

where, M is the molecular mass, and V is the volume per atom. If θ_{Dn} represents the Debye temperature of

nanoparticle and θ_{Db} , the Debye temperature of material for corresponding bulk state, then,

$$\frac{\theta_{Dn}^2}{\theta_{Db}^2} = \frac{T_{mn}}{T_{mb}} \quad (13)$$

Again, according to the Debye theory [20, 21], the specific heat for bulk material (C_{pb}) at constant pressure is related to Debye temperature of bulk material, as-

$$C_{pb} \propto \frac{1}{\theta_{Db}^2} \quad (14)$$

and for nanomaterials, the specific heat (C_{pn}) relation will be,

$$C_{pn} \propto \frac{1}{\theta_{Dn}^2} \quad (15)$$

Combining Eqs. (14) & (15), we have (given by Zhu et al. [21])

$$\frac{C_{pn}}{C_{pb}} = \frac{\theta_{Db}^2}{\theta_{Dn}^2} = \frac{T_{mb}}{T_{mn}} \quad (16)$$

Now using Eq. (11) in above expression, we get

$$C_{pn} = C_{pb} \left[1 - 4\alpha \frac{\delta}{\eta} \frac{d}{D} \right]^{-1} \quad (17)$$

A different formula has been proposed by S. Bhatt et al. [22] with the help of a model given by Qi and Wang [12] and is given by,

$$\frac{C_{pn}}{C_{pb}} = \left(1 - 3 \frac{d}{D} \right) = \left[1 - 3 \frac{d}{D} \left(\frac{T_{mb}}{T_{mb} - T_0} \right) \right]^{-1} \quad (18)$$

The size and shape dependence of melting entropy for nanomaterials is given by the following equation [22],

$$S_{mn} = S_{mb} + \frac{3R}{2} \log \left(\frac{T_{mn}}{T_{mb}} \right) \quad (19)$$

where, S_{mn} and S_{mb} are melting entropies of nano and bulk material respectively, R is gas constant. Using Eq. (11), we can write as

$$S_{mn} = S_{mb} + \frac{3R}{2} \log \left(1 - \frac{4\alpha\delta d}{\eta D} \right) \quad (20)$$

The relation between melting entropy and melting enthalpy for bulk material is given by

$$H_{mb} = T_{mb} S_{mb} \quad (21)$$

The properties of the materials at the nano- level varies mostly due to the surface atoms and its interaction with

the core atoms, the effect of these atoms has already been considered in the derivation of earlier expressions. Thus, the above expression of melting enthalpy given in Eq. (21) can be used at nano levels with the consideration of the effect of surface atoms. Hence, we can write

$$H_{mn} = T_{mn} S_{mn} \quad (22)$$

Putting the values of Eqs. (11), (18) and (19), we get

$$H_{mn} = \left[H_{mb} + \frac{3RT_{mb}}{2} \log \left(1 - \frac{4\alpha\delta d}{\eta D} \right) \right] \left(1 - \frac{4\alpha\delta d}{\eta D} \right) \quad (23)$$

3 Result and discussion

The input parameters used in the calculations are tabulated below.

We have considered the samples of Silver (Ag), Palladium (Pd), Indium (In), Copper (Cu), Aluminium (Al), and Nickel (Ni) to study the variation of their thermophysical properties related to its shape and size. The input data required for computation, are taken from the Tables 1 and 2. We have calculated the values of specific heat (C_{pn}), melting entropy (S_{mn}), and melting enthalpy (H_{mn}) for spherical ($\alpha = 1$) nanoparticles at different sizes using Eq. (17), (20), and (23) respectively. We have derived these equations, introducing the effect of packing fraction and relaxation effect, playing an effective role at the different sizes in the nano range. Using this new concept, we have obtained new formula (Equation-17) for the calculation of specific heat at varying sizes of metallic nanoparticles. The obtained results are compared with available experimental data. The values of specific heat at varying sizes of metallic nanoparticles of Ag, Pd, Cu, and Ni has been computed using Eq. (17). From Eq. (11) the melting temperature decreases with the decreasing size of nanoparticle and therefore from Eq. (17), specific heat increases as the size of nanoparticle decreases. Computed results for the above samples are shown in Fig. 1, 2, 3, 4. This variation is prevalent below the size of 30 nm, after this size the variation is almost negligible. The reason for increasing the specific heat of nanoparticle is due to the increase in thermal vibration of surface atoms at the nano level. At the lower size, there are a greater number of surface atoms which require more heat to make a balance between thermal vibration and increment in the temperature of the nanomaterials. Moreover, at the lower sizes, the structure of the nanomaterials may change due to the variation in the lattice parameters.

Using similar concept, we have also derived Eq. (20) to compute the melting entropy of the samples Cu, Al, Ag and

Table 1 Input parameters for the selected samples such as atomic diameter [23], specific heat, melting enthalpy, melting entropy and melting temperature [24–26]

Metals	Atomic diameter (nm)	Specific heat (J/mole-K)	Melting enthalpy (kJ/mole)	Melting entropy (J/mole-K)	Melting temperature (K)
Silver(Ag)	0.3197	25.35	11.30	9.16	1235
Copper(Cu)	0.2822	24.47	13.26	9.76	1358
Indium(In)	0.3686	26.74	3.29	7.65	429.8
Palladium(Pd)	0.3040	25.98	17.6	–	1827
Nickel(Ni)	0.2751	26.07	17.2	–	1728
Aluminum (Al)	0.3165	11.46	10.7	11.46	933.3

Table 2 The shape factor for different structures [5]

Particle shape	Shape factor(α)
Spherical	1
Regular tetrahedral	1.49
Regular hexahedral	1.24
Regular octahedral	1.18

In nanoparticle. The computed values of melting entropy for these samples have been calculated using Eq. (20) and compared with the experimental values at their different size range. The variation of calculated and experimental values has been depicted in Fig. 5, 6, 7, and 8. One more important thermophysical property, melting enthalpy, has

also been studied using the above said new concept given in Eq. (23). We have computed the melting enthalpy for the metallic nanoparticles of Ag, Cu, and In. The obtained values are compared with their experimental values which are depicted in Fig. 9, 10, and 11. From the computed results it is obvious that the melting entropy (S_{mn}) and melting enthalpy (H_{mn}) of nanoparticles decrease with the decreasing size of nanoparticle. This is also observed that the decrement is dominated below 25 nm. Since the nanoparticles having a lower size will have a greater number of surface atoms so they will be more stable in comparison of greater sizes. Thus, the smaller nanoparticles require more energy to increase the melting entropy and thermal enthalpy. Further, the explanation of the above thermophysical properties of nanoparticles including the

Fig. 1 Variation of specific heat of Ag nanoparticles with size. Experimental values [27] are shown by black circles **Fig. 2** Variation of specific heat of Pd nanoparticles with size. Experimental value [28] is shown by black circle

Fig. 3 Variation of specific heat of Cu nanoparticles with size **Fig. 4** Variation of specific heat of Ni nanoparticles with size **Fig. 5** Variation of melting entropy of Cu nanoparticles with size. Experimental values [29] are shown by black circles **Fig. 6** Variation of melting entropy of Al nanoparticles with size. Experimental values [30] are shown by black circles

Fig. 7 Variation of melting entropy of Ag nanoparticles with size. Experimental values [31] are shown by black circles

Fig. 8 Variation of melting entropy of In nanoparticles with size. Experimental values [32] are shown by black circles

Fig. 9 Variation of melting enthalpy of Ag nanoparticles with size. Experimental values [25] are shown by black circles.

Fig. 10 Variation of melting enthalpy of Cu nanoparticles with size. Experimental values [29] are shown by black circles

Fig. 11 Variation of melting enthalpy of In nanoparticles with size. Experimental values [32] are shown by black circles

dangling bond effect, the number of surface atoms, and the effect of their thermal vibration at the lower size has been given in the further discussions of this section.

The graph shown in Figs. 1, 2, 3 and 4 suggests that the specific heat of metallic nanoparticles varies inversely with their size. The specific heat of selected nanoparticles decreases with their increasing size. From the graphs, it is also clear that at a very low range of size of metallic nanoparticles, the specific heat becomes large enough as compared to their corresponding bulk values. There is a sharp change (increase) in the specific heat for selected samples below 15 nm. The calculated values of specific heat using Eq. (17) are in good agreement with the experimental values. We have also compared our present model with the existing model suggested by S. Bhatt et al. [22] from which our model can predict more accurate values. It means the earlier model needs modification as per the effective role of structural change and relaxation factor at the nano level. In our suggested model, the shape of Ag nanoparticle are taken spherical ($\alpha = 1$). In the present case of silver, the relaxation factor δ , defined by the ratio of dangling bond to the total bonds of the atom, has been taken 1/3 and 1/4 both. It is observed that our computed values are in good agreement with the experimental values for $\delta = 1/3$. In the case of Pd, the available experimental data is found closer to the graph with relaxation factor $\delta = 1/2$. Good agreement of our results encourages us to predict the behaviour of specific heat with its varying size of other metallic nanoparticles for which the experimental data is not available. We have predicted the variation of specific heat of Cu and Ni nanoparticles with their varying size for $\delta = 1/2$ and $1/3$, which has been given in Fig. 3 and 4. With the analogy of fcc structure as in case of Ag & Pd, the expected variation of specific heat will be observed between $\delta = 1/2$ and $1/3$, the experimental verification for Cu and Ni nanoparticles is still required.

We know that the melting entropy is also an important thermophysical property of materials. The proposed formula, given by Eq. (20), describes the change in melting entropy of nanoparticles with their size, shape, and

structure. Figure 5 shows the variation of melting entropy of Cu nanoparticles by taking $\alpha = 1$ and $\delta = 1/2$ and $1/3$. The predicted values for $\delta = 1/3$ are in good agreement with the experimental values. In the case of Al nanoparticles (Fig. 6), the predicted values of melting entropy are in good agreement with the experimental values on consideration of $\alpha = 1$ and $\delta = 1/2$ (at lower range) and at $\delta = 1/3$ (beyond 15 nm). The computed values of melting entropy for Ag nanoparticles have good consistency with experimental values on taking $\alpha = 1$ and $\delta = 1/4$, which have been shown in Fig. 7. If we take the case of indium, the predicted values for melting entropy given by Eq. (20) agree with available experimental data for relaxation factor lying between $\delta = 1/2$ and $1/3$, as shown in Fig. 8.

Another important thermophysical property, melting enthalpy (H_m), is also calculated for silver, copper, and indium nanoparticles. Figure 9 shows the variation of melting enthalpy of silver nanoparticles with their varying sizes. Here, again, we have taken the shape factor $\alpha = 1$ and relaxation factor $\delta = 1/3$ and $1/4$. It is obvious from the above graph, the proposed formula, given by Eq. (23), strongly agrees with the available experimental data for $\delta = 1/3$ which proves the validity of the formula at the nano level. The melting enthalpy of silver nanoparticles decreases with the decrease in the size of nanoparticles. This formula is also applied for the Cu nanoparticles. For this sample, we have considered, the shape factor $\alpha = 1$ and relaxation factor $\delta = 1/2$ and $1/3$. From our computed results, it is observed that the proposed formula for the calculation of melting enthalpy of copper nanoparticle, the suitable values of δ lying between $1/2$ and $1/3$ as shown in Figs. 10, 11 shows the variation of melting enthalpy of indium nanoparticles considering $\alpha = 1$ and $\delta = 1/2$, $1/3$ and $1/4$. It is obvious from the plot that our computed results are in good agreement with the experimental values. Below 10 nm, the predicted graph for $\delta = 1/3$ agrees with experimental values while beyond this range the choice of $\delta = 1/4$ is more suitable. A similar explanation regarding the variation of thermophysical properties of

nanoparticles and the effect of their shape and sizes has also been given by different researchers [14, 33, 34].

4 Conclusion

A qualitative and reasonable model for describing the dependence of thermophysical properties on the size, shape, and structure of the metallic nanoparticles has been proposed using the appreciable effect of relaxation factor and packing fraction of crystal. It is found that the specific heat of nanomaterials increases with a decrease in their size but the melting entropy and melting enthalpy are lowered as the size of nanomaterials is decreased. It is also, observed that the relaxation factor has a major effect on these thermophysical properties which help us to understand these properties at the nano level. The calculated values of different thermophysical properties like specific heat, melting enthalpy, and melting entropy using our present model, are in good agreement with their experimental values. Thus, the proposed model can be used to predict the thermophysical properties of other nanomaterials up to the desired shape and size of nanomaterials.

Declarations

Conflicts of interest The authors declare that they have no conflict of interest

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