ANALYTICAL MODEL FOR THE SIZE DEPENDENT MELTING ENTROPY AND ENTHALPY OF NANOMATERIALS

Mehul Manu¹ Mahipal Singh² and Vikash Dubey³

¹²Department of Physics, R. H. Government P.G. College Kashipur, Kumaun University, Nainital, Uttarakhand, India
³Department of Physics, P. N. G Government P. G. College Ramnagar, Kumaun University, Nainital, Uttarakhand, India

Abstract- A simple, analytical model for the size dependent melting entropy and enthalpy is discussed by considering the cubo-octahedral structure with the change of the cluster size in the low dimension scale. Using the model, melting entropy and enthalpy of Ag, Al, Cu, Au, Ni and Pb nanomaterials are calculated as a function of cluster size. An increase in melting entropy and enthalpy of nanomaterials is observed with their size. The melting entropy and enthalpy of the nanomaterials increases as the cluster size increases because of a growing fraction of the surface atom which have large mean square displacement. This brings the entropy and enthalpy of solid nanomaterial closer to the liquid state entropy and enthalpy, and leads to decrease in melting entropy and enthalpy as nanomaterial size is reduced. A comparison between theoretical prediction with other theoretical model like as Qi’s, Jiang’s and Guisbiers model with the available experimental and simulation data. Reasonable agreement between the model prediction and the experimental data is found.

Keywords-Nanomaterials, melting entropy, melting enthalpy, cubo-octahedral, nanosolid.

I. INTRODUCTION

Systems with typical dimensions in the range of 1 to 100 nm are in the intermediate state between the solid and the molecular ones. Such systems are characterized by the fact that the ratio of the number of surface to volume atom is not small. This is known to lead to size and shape effects on the melting entropy and enthalpy of nanomaterials [1]. For the first time, Takagi [2] demonstrated that ultra-fine metallic particle melts below their corresponding bulk melting temperature. It is known that the melting of metallic nanoparticles depends on their size [3-8]. Particularly a complete understanding of the melting transition in nanomaterials cannot be obtained without a clear understanding of the entropy of the melting, which reflects the change in the degree of order upon melting. Eckert et al. [9] have experimentally studied the size dependence of entropy and enthalpy of melting for Al nanomaterial. They observed an increase in entropy of melting with the size of the nanomaterial. Safaei et al. [10] studied the melting entropy and enthalpy of Ag nanomaterial experimentally and observed an increase in those with the particle size. Jiang et al. [11] demonstrated a simple model for the study of melting entropy of nanomaterials and observed that the entropy of melting for nanomaterials decreases as size decreases. Zhang et al. [12] observed the effect of nanoparticle size on the melting enthalpy and found that melting enthalpy of nanomaterials decreases more strongly than a linear relationship of reciprocal of radius to nanomaterials. Jiang et al. [13] studied melting enthalpy depression of nanomaterials. They observed that although the melting temperature has an approximate linear relationship with reciprocal of the radius of nanomaterials, however, there is a divergence from the linearity for the melting enthalpy especially when the radius of the nanomaterials decreases to the microscopic size range. Delogu [14] studied the melting entropy of Cu nanomaterial and observed an increase in melting entropy to increase in particle size of the nanomaterial. Ao et al. [15] discussed the melting enthalpy of Ag nanomaterial with particle size. They reported that melting enthalpy decreases with reduction in grain size. Lou et al. [16] explained the size-dependence on melting entropy and enthalpy of Ag nanomaterial and observed
that melting entropy and enthalpy both of the Ag nanomaterial decreases regularly to decrease in particle size. Guisbiers et al. [17] developed a simple model to define the size-dependent melting enthalpy of nanostructured materials with any adjustable parameter and found an increase in melting enthalpy with an increase in particle size.

Sufficient studies on nanomaterials size-dependent melting entropy and enthalpy are still lacking. In other theoretical models, the crystal order for nanomaterials have not been considered, as it plays a vital role in these studies. One of the most critical characteristics of nanomaterials is their very high surface to volume ratio. When the concentration of building blocks (atom or ions) of a solid becomes sufficiently high, they accumulate into small clusters through homogeneous nucleation. With continuous supply of the building blocks, these clusters tend to coalesce and grow to form a large cluster assembly. The cluster may be considered as an onion-like structure formed by several concentric shells around the central site. All the surface site, which may belong to various shells, are defined as crusts, the number of crusts, \( n \), defines the order of the cluster [18]. Therefore, in this paper, we have planned to study the size effect on melting entropy and enthalpy of nanomaterials by considering the effects of cluster order. For this purpose, Ag, Au, Al, Cu, Ni and Pb nanomaterials have been used.

II. THEORETICAL MODEL

The total cohesive energy of the nanomaterials is the sum of the contribution of the interior atoms and the surface atoms of the nanomaterial, which is expressed as [19]

\[
E_{\text{total}} = E_0(N - N_s) + \frac{1}{2}E_0N_s
\]  

where \( N \) is the total number of the atoms, \( N_s \) is the total number of the surface atoms on the surface of the nanomaterial and \( (N - N_s) \) represents the total number of interiors atoms. \( E_0 \) is the cohesive energy of the bulk material per atom. Therefore, above equation may be expressed as

\[
E_n = E_b \left(1 - \frac{N_s}{2N}\right)
\]

where \( E_n \) is the cohesive energy per mole and is equal to the \( AE_{\text{total}}/N \), where \( A \) is the Avogadro’s number, \( E_b (= AE_0) \) is the cohesive energy per mole of the corresponding bulk material. It is well known that both the cohesive energy and temperature are the parameters to describe the bond strength of the materials and shows the linear relation with each other [20,21], therefore we can write the relation for melting temperature of nanomaterials in terms of surface to volume ratio

\[
T_{mn} = T_{mb} \left(1 - \frac{N_s}{2N}\right)
\]

We are going to consider the value of \( N_s/N \) for cubo-octahedral structure. Clusters with a small number of atoms crystallized in the form of cubo-octahedral structure [18]. Therefore, surface to volume ratio \( N_s/N \) for cubo-octahedral structures as a function of cluster order \( n \) is given as [20]

\[
N_s = \frac{30 \pi^2 + 6}{10n^3 + 15n^2 + 11n + 3}
\]

(4)

where \( N \) is the total number of atoms of nanomaterials and the number of its surface atom is \( N_s \). Consequently \( N_s/N \) is the surface to volume ratio of the nanomaterials and \( n \) is the cluster order of the nanomaterials. Cluster order \( n \) is written in terms of cluster size and atomic size as [22]

\[
n = \frac{1}{2}\left(\frac{r}{r_0} - 1\right)
\]

(5)

where \( r \) is the cluster size radius and \( r_0 \) is atomic radius of the nanomaterials

Surface to volume ratio is depends upon the cluster size radius and atomic radius of nanomaterials, so with the help of Eq. (4), the Eq. (5) takes the form

\[
N_s = \frac{30(r/r_0 - 1)^2 + 24}{(r/r_0)^2 + \gamma}
\]

(6)

The \( N_s/N \) can be written in terms of the cluster size \( (D) \) and atomic size \( (d) \)
\[ N_s = \frac{30(D-1)^2 + 24}{r_0^2 \left[ 5 \left( \frac{D}{d} \right)^2 + 7 \right]} \]  

(7)

(Since \( r_0 = \frac{d}{2} \) and \( r = \frac{D}{2} \))

where \( d \) is atomic diameter and \( D \) is cluster size of the nanostructured materials

The bulk vibrational entropy of melting of bulk is related to melting temperature \( T_{mb} \) by the relation as [23]

\[ \Delta S_{mb} = \frac{3R}{2} \ln \left( \frac{T_{mb}}{C} \right) \]

where \( C \) is a constant and \( R \) denotes the gas constant

On applying for nanosize, the above equation becomes

\[ \Delta S_{mn} = \frac{3R}{2} \ln \left( \frac{T_{mn}}{C} \right) \]

(8)

From equations (1) and (2), the size-dependent melting entropy of a nanostructured materials is

\[ \Delta S_{mn} = \Delta S_{mb} + \frac{3R}{2} \ln \left( \frac{T_{mn}}{T_{mb}} \right) \]

(9)

Using equations (4) and (5) above equation becomes

\[ \Delta S_{mn} = \Delta S_{mb} + \frac{3R}{2} \ln \left( 1 - \frac{15(D-1)^2 + 12}{\frac{D}{d} \left[ 5 \left( \frac{D}{d} \right)^2 + 7 \right]} \right) \]

(10)

The melting enthalpy of a bulk metallic crystal is related with the melting entropy and melting temperature as

\[ \Delta H_{mb} = \Delta S_{mb} T_{mb} \]

(11)

The melting temperature of nanomaterial may be written as

\[ \Delta H_{mn} = \Delta S_{mn} T_{mn} \]

(12)

Combining Eqs. (10) and (11), we get the following relation

\[ \frac{\Delta H_{mn}}{\Delta H_{mb}} = \left( \frac{\Delta S_{mn}}{\Delta S_{mb}} \right) \left( \frac{T_{mn}}{T_{mb}} \right) \]

(13)

Using Eqs. (9) and (10), the Eq (12) yields

\[ \Delta H_{mn} = \left[ \Delta H_{mb} + \frac{3RT_{mb}}{2} \ln \left( 1 - \frac{15(D-1)^2 + 12}{\frac{D}{d} \left[ 5 \left( \frac{D}{d} \right)^2 + 7 \right]} \right) \right] \left[ 1 - \frac{15(D-1)^2 + 12}{\frac{D}{d} \left[ 5 \left( \frac{D}{d} \right)^2 + 7 \right]} \right] \]

(14)

(15)

Eq. (11) and Eq. (15) are the modified equation for melting entropy and enthalpy of different nanomaterials. Obviously, these equations have been derived by considering cubo-octahedral structure on nanomaterials in including cluster order \( n \) in terms of the size of the nanomaterials. Thus, we can use the Eq. (11) and Eq. (15) to study the entropy and enthalpy for different cluster size.

III. RESULT AND DISCUSSION

Nanomaterials can have different geometrical shapes such as cubo-octahedral (co), icosahedra (ico), body-centered cubic (bcc) and simple cubic (sc). Clusters with a small number of atoms crystallized in the form of ico. The structure becomes unstable for a large number of atoms and transforms to cubo-octahedral. One of the most critical characteristics of nanoparticles is their very high surface to volume ratio. When the concentration of atom or ions of a solid becomes sufficiently high, they accumulate into small clusters through homogeneous nucleation. With continuous supply of the building blocks, these clusters tend to coalesce and grow to form a large cluster assembly. The cluster may be considered as an onion-like structure (non-spherical) formed by several concentric shells around the central site. All the surface site, which may belong to various shells, are defined as crusts, the number of crusts, \( n \), defines the order of the cluster [18,22]. Keeping in mind these facts, a simple theoretical model has been developed to study the melting entropy and enthalpy of nanomaterials with their cluster size. For this purpose, we have used the Eqs. (11) and (15).
The input data used in calculation is given in Table 1. The results came from Eq. (11) for the entropy with the respect of cluster size of Ag nanomaterial is plotted in figure 1. The entropy of the Ag nanomaterial increases with increasing the cluster size, the increment in entropy is higher with the cluster size below 12nm and the increment in entropy becomes slower above 12 nm. The theoretical result is compared with the Jiang model and available experimental and simulation data. The trend of our model similar to the Jiang model and has excellent agreement with available experimental and simulation data.

Table 1: Input parameter used in the theoretical calculation

<table>
<thead>
<tr>
<th>Nanoparticle</th>
<th>d (nm)</th>
<th>$T_{mb}$ (K) [28]</th>
<th>$\Delta H_{mb}$ (kJ/mol) [29]</th>
<th>$\Delta S_{mb}$ (J/mol-K) [29]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>0.2880 [30]</td>
<td>1234.93</td>
<td>11.3</td>
<td>9.15</td>
</tr>
<tr>
<td>Au</td>
<td>0.2884 [30]</td>
<td>1337.33</td>
<td>12.5</td>
<td>9.35</td>
</tr>
<tr>
<td>Al</td>
<td>0.2860 [30]</td>
<td>933.47</td>
<td>10.7</td>
<td>11.47</td>
</tr>
<tr>
<td>Cu</td>
<td>0.2560 [31]</td>
<td>1357.77</td>
<td>13.1</td>
<td>9.65</td>
</tr>
<tr>
<td>Ni</td>
<td>0.2480 [26]</td>
<td>1728.00</td>
<td>17.2</td>
<td>9.95</td>
</tr>
<tr>
<td>Pb</td>
<td>0.3870 [27]</td>
<td>600.61</td>
<td>4.77</td>
<td>7.94</td>
</tr>
</tbody>
</table>

The variation in entropy with the cluster size and shape of Al calculated from Eq. (11) is shown in figure 2. From the figure, the entropy of Al nanomaterial decreases with decreasing the cluster size. For the comparison our model, we plotted Jiang model and simulation results. It is clear from the graph; the trend of entropy of Al nanomaterial is similar the Jiang model and good agreement with simulation results.

![Figure 1](image1.png)

**Figure 1.** The melting entropy is the function of cluster size of Ag nanomaterial. The solid lines represent the different model predictions and our model based on Eq. (11) for Ag nanomaterial.

![Figure 2](image2.png)

**Figure 2.** The melting entropy is the function of cluster size of Al nanomaterial. The solid lines represent the different model predictions and our model based on Eq. (11) for Al nanomaterial.
From Eq. (11), we have calculated the size dependent entropy of Cu nanomaterial with increasing cluster size. The theoretical results obtained by Eq. (11) are reported in figure 3 along with the available experimental data. Figure predicted that the melting entropy increases with increasing the cluster size of nanomaterial. There are good agreements between the model prediction with other theoretical model i.e. Jiang with the available experimental data. A good agreement between the model with the other theoretical and experimental data convinced the author to extend the model for the study of entropy of Au, Ni and Pb nanomaterials for which the simulation and experimental data are not available.

Figure 3. The melting entropy is the function of cluster size of Cu nanomaterial. The solid lines represent the different model predictions and our model based on Eq. (11) for Cu nanomaterial.

Figure 4. The melting entropy is the function of cluster size of Au nanomaterial. The solid lines represent the different model predictions and our model based on Eq. (11) for Au nanomaterial.
Figure 5. The melting entropy is the function of cluster size of Ni nanomaterial. The solid lines represent the different model predictions and our model based on Eq. (11) for Ni nanomaterial.

Figure 4 represents the entropy of Au nanomaterial calculated by Eq. (11). For comparison purpose, we also show the results obtained theoretically by Jiang et al. The trend of our model is similar to the results obtained by Jiang et al.

Figures 5 and 6 compare the model prediction of Ni and Pb nanomaterials. Our model prediction is consistent with the Jiang model and is found to decrease with a decrease in cluster size.

In sum, we have used Eq. (11) to predict the size dependent melting entropy of Ag, Au, Al, Cu, Ni and Pb nanomaterials. The results obtained are shown in figures 1-6. It is obvious from the figures that the melting entropy of nanomaterials increases with increase in cluster size. The figures compare the model prediction with Jiang model and the experimental observation for the size dependent melting entropy of various nanomaterials. It is evident that the model prediction is consistent with the experimental observations—melting entropy increases with increase in particle size. Melting entropy represents the difference between the solid-state entropy and the liquid state entropy. The entropy of solid increases as the nanomaterial size decreases because of a growing fraction of the surface atom which have large mean square displacement \[24\]. This brings the entropy of solid nanomaterial closer to the liquid state entropy and leads to decrease in melting entropy as cluster size is reduced.

Figure 6. The melting entropy is the function of cluster size of Pb nanomaterial. The solid lines represent the different model predictions and our model based on Eq. (11) for Pb nanomaterial.
The size dependent melting enthalpy for Ag nanomaterial is shown in figure 7 along with the other theoretical model named as Jiang, Guisbiers and the experimental data reported by Safaei et al. [10]. In this experiment Safaei et al. observed that the melting entropy of Ag nanomaterial is increased with increasing the particle size. From the figure, our model trends are an excellent match with Guisbiers model and experimental data and saw a variation with Jiang et al.

We used Eq. (15) to calculate the melting enthalpy of Al nanomaterial. Figure 8 shows a comparison between the model with Jiang, Guisbiers and experimental data. Our model is excellent agreement with Guisbiers model little deviations with the experimental data.

We used Eq. (15) to calculate the melting enthalpy of Cu nanomaterial. Figure 9 shows a comparison between the model with Jiang, Guisbiers and experimental data. Our model is excellent agreement with Guisbiers model little deviations with the experimental data.
Using Eq. (15), we calculated the melting enthalpy of Cu nanomaterial as the function of cluster size. The result is reported in figure 9. The melting enthalpy is found to decrease with the decrease of cluster size. Figure 9 along with the molecular simulation result, which support the prediction on the melting enthalpy of Cu nanomaterial. There is good agreement with the simulation results which support the validity of the present work.

Figure 10 The melting enthalpy is the function of cluster size of Au nanomaterial. The solid lines represent the different model predictions and our model based on Eq. (15) for Au nanomaterial.

Figure 11 The melting enthalpy is the function of cluster size of Ni nanomaterial. The solid lines represent the different model predictions and our model based on Eq. (15) for Ni nanomaterial.

Figure 12 The melting enthalpy is the function of cluster size of Pb nanomaterial. The solid lines represent the different model predictions and our model based on Eq. (15) for Pb nanomaterial.
Eq. (15) is used to calculate the size dependent melting enthalpy of Au, Ni and Pb nanomaterials. The computed values of melting enthalpy of Au, Ni and Pb are shown in figure 10-12 along with the other theoretical model in the absence of experimental data. As revealed from the figure, the melting enthalpy decreases with the decrease in the cluster size. The melting temperature decreases sharply with a small reduction in cluster size. Finally, using Eq. (15), we have calculated the melting enthalpy of nanomaterials as a function of their size. The results obtained have been plotted in figures 7-12. It is obvious from the figures that the melting enthalpy of nanoparticle increases with reduction in the cluster size. It is evident that the model predictions are consistent with other theoretical model (i.e. Jiang and Guisbiers model) experimental observations- melting enthalpy increases with increase in cluster size. For nanomaterial confined in nanopores, when there is a chemical interaction between the confined particles and pore walls, melting enthalpy changes depending on binding energy changes between interface molecules and internal molecules [25]. We can say that the energetic change originated from the atom/molecule binding state at the interface may be essential to the melting enthalpy change. Thus, the inclusion of cubo-octahedral structure in the model, improves the theoretical results on melting entropy and enthalpy. A reasonable agreement between our model predictions and the experimental data has been found. Seeing the potential of the model, the other properties of nanomaterial like specific heat, thermal conductivity, energy band gap, susceptibility, Curie temperature, Neel temperature etc. can be studied. The work in this direction is in progress.

IV. CONCLUSION

In conclusion, based on the cubo-octahedral structure, a theoretical model for the size dependent melting entropy and enthalpy of the low dimension scale is developed. Using the model, melting entropy and enthalpy of Ag, Al, Cu, Au, Ni and Pb nanomaterials are calculated as a function of cluster size. The melting entropy is calculated by Eq. (11) and Eq. (15) for considering nanomaterials. An increase in melting entropy and enthalpy is observed as the cluster size increases. The results came from Eq. (11) and Eq. (15) compared with other theoretical model in which ideal sphere concept is taken but in our model, we considered atom non-spherical approach taking as cubo-octahedral structure. Thus, the inclusion of cubo-octahedral structure in the model, improves the theoretical results on melting entropy and enthalpy. A reasonable agreement between our model predictions and the experimental and simulation data has been found.

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