



Study of Melting Temperature Depression in Nanoparticles with their Size using Cluster Order Concept

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Abstract: A new model, based on cluster order calculations, has been developed for the study of melting temperature depression in nanoparticles with their size. Cluster order plays a crucial role in determining various properties of nanoparticles. Using this model, melting temperature of Al, Ag, Au and Sn nanoparticles has been calculated. Melting temperature depression of these nanomaterials has been observed as the particle size decreases. Our theoretical predictions agree well with available experimental and other theoretical results which supports the validity of present model.

Keywords: Size effect, Melting temperature, Nanoparticles, Cluster order

I. Introduction

Melting temperature depression is the phenomenon of reduction of the melting temperature of a material with reduction of its size. This phenomenon is very prominent in nanoscale materials which melt at temperatures hundreds of degrees lower than bulk materials. The melting temperature of a bulk material is not dependent on its size but as the dimensions of a material decreases towards the atomic scale, the melting temperature scales with the material dimensions. The decrease in melting temperature can be on the order of tens to hundreds of degrees for metals with nanometer dimensions [1-3]. Melting temperature depression is most evident in nanowires, nanotubes and nanoparticles which all melt at lower temperatures than bulk amounts of the same material. Nanoparticles are easiest to study due their ease of fabrication and simplified conditions for theoretical modeling.

It has been well established both experimentally and theoretically that the melting temperature of nanoparticles depends on the particle size [1, 4-8]. Wronski [9] studied the size dependence of the melting temperature of tin nanoparticles by means of transmission electron diffraction and microscopy. He found that the melting temperature of a spherical particle of tin (Sn) decreases as the radius of the particle decreases. Jiang et al. [10] and Chang-dong et al. [11] synthesized Sn nanoparticles of various sizes via chemical reduction method and they observed particle size dependent melting temperature. Their results showed that different sized Sn nanoparticles had different melting point depression behavior. Sun et al. [12] and Liang et al. [13] studied the size dependence of melting temperature of Al nanoparticles. Cottie [14] performed the size dependence of melting temperature of nanocrystalline Au. Eckert et al. [15] and Lai et al. [16] studied the effect of size on melting temperature of Al nanoparticles experimentally. Buffat and Borel [17] studied the melting temperature of Au nanoparticle. In all these experiments, the experimentalists observed a depression in melting temperature of these nanoparticles as the particle size decreases. The size- dependent melting properties of Sn [18], Ag [19], Al [20] and Au [21] nanoparticles have been studied both on experiment and theory.

There are some other theoretical work on melting temperature of nanoparticles. Kumar and Kumar [22] used a model to study the size dependence of melting temperature of Au, Al, Ag etc. nanoparticles. They found that the melting temperature of these nanoparticles decreases with decrease in particle size. Arora and Joshi [23] discussed a thermodynamic analytic model to study the size effect on melting temperature of Al, Ag, Au and Sn nanometals and found the melting temperature shows decreasing trend with decrement in size of the nanomaterial.

It is very much evident from the above that various experimental and theoretical studies have been performed to study the melting temperature of nanoparticles with particle size but in all these studies the crystal order of the materials has not been considered as it plays very important role in this study. When the concentration of building blocks (atoms or ions) of a solid becomes sufficiently high, they aggregate 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. Clusters are structures with a central site around which the cluster is grown. The cluster may be considered as an onion-like structure formed by several concentric shells around the central site. All the surface sites which may belong to various shells are defined as crusts. The number of crusts (n) defines the order of the cluster [24]. It is, therefore, interesting to study the melting temperature of nanoparticles with the inclusion of the effect of the cluster order. This encouraged the author to study the melting temperature depression

in nanoparticles with particle size using cluster order concept. Here we have considered simple cubic (sc) cluster structure of nanoparticles.

II. Theoretical Analysis

For a simple cubic (sc) cluster, the equation for melting temperature of a nanomaterial is given as [24]:

$$T_{mp} = T_{mb} \left(\frac{2n}{2n+1} \right) \quad (1)$$

where T_{mp} and T_{mb} are the melting temperature of the nanoparticle and the corresponding bulk material. 'n' is the cluster order(number of crusts).

Cluster order 'n' is given as [24]:

$$n = \frac{1}{2} \left(\frac{r}{r_0} - 1 \right) \quad (2)$$

where 'r' is the particle size (radius) and 'r₀' is the atomic radius of the nanoparticle.

Using Eq.(2), the Eq.(1) takes the form:

$$\begin{aligned} T_{mp} &= T_{mb} \left[\frac{2 \times \frac{1}{2} \left(\frac{r}{r_0} - 1 \right)}{2 \times \frac{1}{2} \left(\frac{r}{r_0} - 1 \right) + 1} \right] \\ &= T_{mb} \left[\frac{\left(\frac{r}{r_0} - 1 \right)}{\left(\frac{r}{r_0} - 1 \right) + 1} \right] = T_{mb} \left[\frac{\frac{r}{r_0} - 1}{\frac{r}{r_0}} \right] \end{aligned}$$

Or

$$T_{mp} = T_{mb} \left(\frac{r_0}{r} \right) \left(\frac{r}{r_0} - 1 \right) \quad (3)$$

But $r_0 = d/2$ and $r = D/2$, where 'd' is the atomic diameter and 'D' is the particle diameter.

Therefore Eq.(3) becomes:

$$\begin{aligned} T_{mp} &= T_{mb} \left(\frac{\frac{d}{2}}{\frac{D}{2}} \right) \left(\frac{\frac{D}{2}}{\frac{d}{2}} - 1 \right) \\ &= T_{mb} \left(\frac{d}{D} \right) \left(\frac{D}{d} - 1 \right) \end{aligned}$$

Or

$$T_{mp} = T_{mb} \left(\frac{d}{D} \right) \left(\frac{D}{d} - 1 \right) \quad (4)$$

The Eq.(4) is the model which is used to study melting temperature depression in nanoparticles with particle size. Obviously, the above equation has been established by including the effect of cluster order 'n' in terms of the particle size.

III. Results and Discussion

From Eq.(4), melting temperature of nanoparticles can be obtained. Here, we have considered Sn, Al, Ag and Au nanoparticles with simple cubic (sc) structure. The input parameters used in present work are given in Table 1.

Table 1: Input parameters used in calculations [25-27]

Nanomaterial	T_{mb} (K)	Atomic diameter (d) in nm
Sn	505.10	0.3724
Al	933.25	0.2460
Ag	1234.00	0.2880
Au	1337.6	0.3188

Using Eq.(4) and input parameters shown in Table 1, the values of melting temperature (T_{mp}) of Sn, Al, Ag and Au nanoparticles have been calculated for particle size (D). The computed values of melting temperature (T_{mp}) of these nanoparticles have been plotted against varying size of nanoparticle in Fig. 1, 2, 3 and 4 respectively alongwith the available experimental results [11] and theoretical data [23].

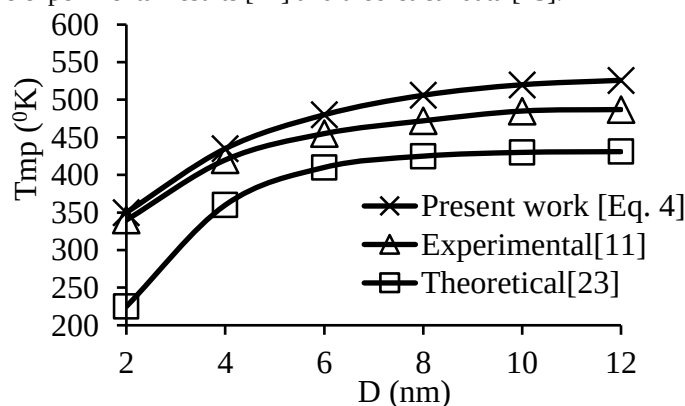


Fig. 1: Size-dependent melting temperature of Sn nanopai

Fig.1 shows size dependence of melting temperature of Sn nanoparticle in sc crystal structure. It is obvious from the figure that the melting temperature of Sn nanoparticle decreases with decrease in particle size. There is good agreement between our theoretical results and experimental results [11].

Fig.2 represents the variation of melting temperature of Al nanoparticle with particle size. Similarly, it is found that the melting temperature of Al nanoparticle decreases as the particle size decreases. It is also clear that our theoretical results are in good agreement with available experimental data [16].

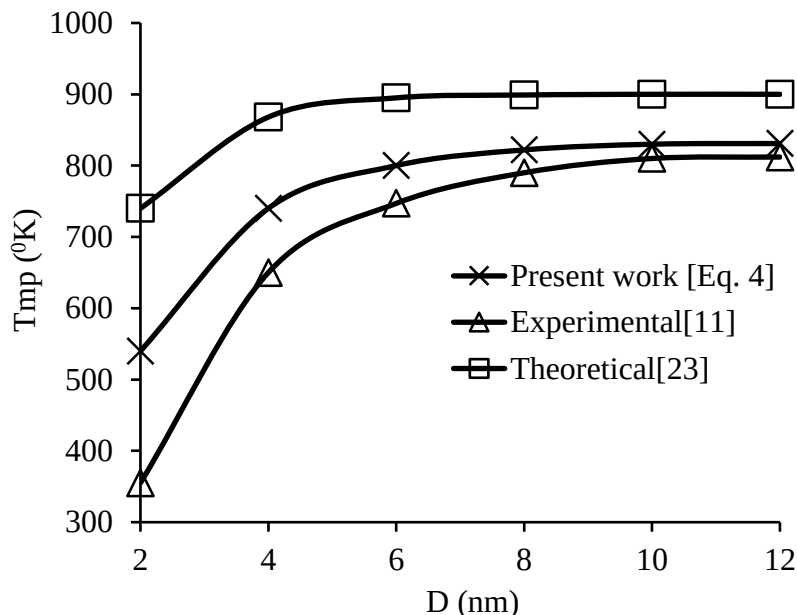


Fig. 2: Size-dependent of melting temperature of Al nanoparticle

Fig.3 illustrates the size-dependent melting temperature of Ag nanoparticle. It can be seen from the figure that melting temperature of Ag nanoparticle is size-dependent and it decreases as the particle size decreases. It can be seen that our theoretical results on melting temperature are in reasonable agreement with experimental data [19].

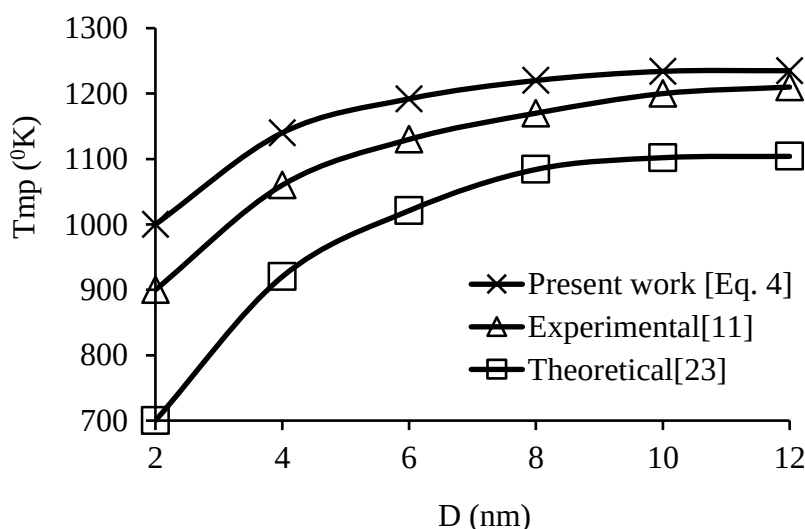


Fig. 3: Size-dependent of melting temperature of Ag nanoparticle

Similarly, Fig.4 predicts size dependence melting temperature of Au nanoparticle. From the figure, it can be clearly seen that with decrease in particle size, the melting temperature reduces. The theoretical results are in good agreement with experimental data [17].

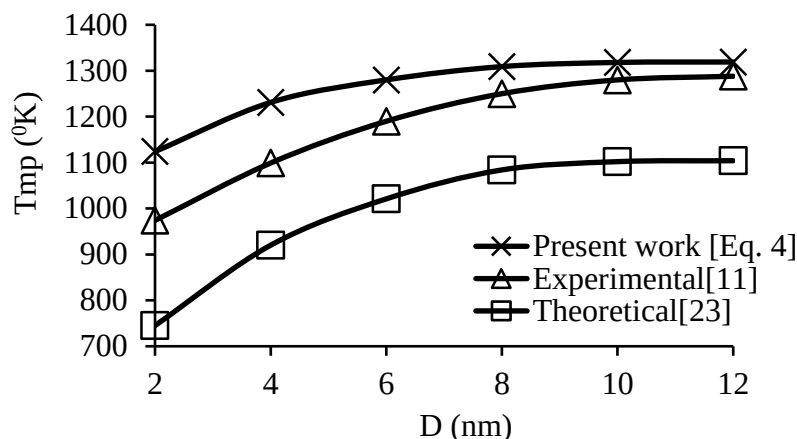


Fig. 4: Size-dependent of melting temperature of Au nanoparticle

All the figures reveal that the melting temperature of Sn, Al, Ag and Au nanoparticles decreases as the particle size reduces. The melting temperature of a nanoparticle decreases sharply as the particle size reaches a critical value, usually < 12 nm. This is due to the high surface area to volume ratio for small particles which as a consequence of the higher surface energy substantially affects the interior bulk properties of the material, resulting in a decrease of the melting temperature. The outer surface of the nanoparticles plays a relevant role in the melting temperature depression [10]. The theoretical results obtained from newly developed model have also been compared with other available theoretical data [23]. It is reported that the inclusion of cluster order in the model improves the theoretical results on melting temperature of these nanoparticles. Hence, we can say that newly developed theoretical model reveals the better results on melting temperature than other models.

IV. Conclusion

In conclusion, new theoretical model based on cluster order calculations has been developed for the study of melting temperature depression in nanoparticles with their size. Using the model, melting temperatures of Sn, Al, Ag and Au nanoparticles in sc cluster structure have been calculated for varying particle size. The computed values of melting temperature of these nanoparticles have been plotted against varying particle size along with available experimental data and other theoretical results. A depression in melting temperature of these nanomaterials with particle size has been observed. The changes in melting temperature occur because of much larger surface-to-volume ratio than bulk materials. The theoretical results on melting temperature are found in reasonable agreement with available experimental data.

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