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ORIGINAL ARTICLE

Theoretical Explanation of Melting Temperature of Nanomaterials

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ABSTRACT

The melting temperature is very fundamental properties of the nanomaterials. The present model is based on the assumption that the clusters of nanomaterials have cubo-octahedral structure and the model has been used to describe the melting temperature of Ni, and Pb metallic nanoparticles. The model is being dealt with the melting temperature of nanosolids, nanowires and nanofilms with free surface and can be dealt with non-free surface also. It is noticed that the melting temperature of the nanomaterials decreases with decreasing of the cluster size due to the creation of instability of the atoms. Nanofilms have higher melting temperature then the nanowires and nanosolids at a particular cluster size due to the larger bond energy between the surface atoms and interior atoms in nanofilms. The results demonstrate that the variation of melting temperature is slant with cluster size above 20 nm while it is sharp with cluster size below 20 nm due to the presence of large surface atoms at D<20 nm. Melting temperature is also depends on the dimension of nanomaterials i.e., lower the dimension of nanomaterials is diminishing the melting temperature. Our results of melting temperature are in good agreement with experimental and simulation data. The tendency of our study is similar to that of Qi's model and Liquid drop model. Hence the present model of melting temperature, which is based on quasi-spherical cluster shape, may have potential application in the research of thermo-elastic properties of the nanomaterials.

***Key words**: Theoretical Explanation, Melting Temperature, Nanomaterials*

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INTRODUCTION

Melting temperature is a basic physical parameter that has a significant impact on thermo-elastic properties. The melting of nanomaterials, as a universal solid-liquid transformation, has been utilized in metallurgy for a long time. On a nanometer scale, as a result of elevated surface to volume ratio, usually the melting temperatures of metallic particles with a free surface decrease with decreasing of their particle sizes. However, the melting temperature of free standing nanometals decreases with decrease in the cluster size. It is known that the melting temperature and the cohesive energy are two parameters to describe the bond strength.

Using a top-down approach, Guisbiers, *et al.* (2008) reported a theoretical investigation of the melting temperature at the nanoscale, for different shapes of "free-standing" nanostructures. Determination in nanostructures was found to be essential for sizes below 100 nm. Hock *et al.* (2008) using first principles density functional theory studied the melting-point depression of free sodium nanoparticles. Nanda (2009) has summarized the important results on the hundred years of thermodynamic model and the melting temperature of nanoparticles. They showed that thermodynamic model with different hypothesis can be applied to understand the variation of melting temperature of

very small sizes without modifying the values of the bulk thermodynamic parameters. Omid *et al.* (2011) reported a theoretical model to predict the size-dependency of melting point for embedded nanoparticles by employing surface and interior average coordination number, cohesive energy and atomic bond strength. The model was applied on the perfect clusters of icosahedral and body centered tetragonal without any vacancies and defects. Kumar *et al.* (2013) studied thermal properties of nanocrystalline materials that can provide vital information on their intrinsic nanostructure characteristics.

ANAYLITICAL MODEL

Qi (2005) proposed a simple analytical equation for the cohesive energy of nanomaterials. According to this equation, the total atoms of a nanosolid denoted as N and the total number of surface atom on the surface of a material is N_s, where the surface atom is considered to the first layer of the nanomaterial. Then the total number of interior atoms is $N - N_s$. If the relaxation of the nanomaterial is not considered, the interior structure is the same as the corresponding bulk materials. Let E_0 be the cohesive energy per atom of the bulk material, the contribution of the central atoms to the cohesive energy of the nanosolids is $E_0(N - N_s)$. Since half of the total bonds of each surface atom are an unsatisfied bond, the contribution of each surface atom to the cohesive energy of nanomaterial should equal to $E_0/2$, and the total surface atoms contribution is $NE_0/2$. The total cohesive energy of the nanomaterials (E_{total}) is the sum of the contribution of the surface atoms and the interior atoms, which is given as-

$$\boldsymbol{E_{total} = E_0(N - N_s) + \frac{1}{2}E_0N_s} \quad \text{...(1)}$$

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

$$\boldsymbol{E_n = E_b\left(1 - \frac{N_s}{2N}\right)} \quad \text{...(2)}$$

where E_n is the cohesive energy per mole and is equal to the AE_{total}/N, where A is the Avogadro's number $E_b(= AE_0)$ signify the cohesive energy of the corresponding bulk material per mole.

However, the value of cohesive energy is different for different shapes that's mean the case is different for nanosolids, nanowires, and nanofilms. Considering these facts, we proposed a general expression of the cohesive energy for different shapes by introducing dimension factor γ

$$\boldsymbol{E_n = E_b\left(1 - \gamma\frac{N_s}{2N}\right)} \quad \text{...(3)}$$

where γ is dimension factor, the value of γ is 1, $2/3$, $1/3$ for nanosolid, nanowire and nanofilm respectively (Nanda, *et al*, 2002).

QUASI-SPHERICAL CONSEDERTION

According to Mirjalili and Khaki (2008) the mathematical expression of surface to volume N_S/N ratio of cubo-octahedral is expressed as-

$$\boldsymbol{\frac{N_s}{N} = \frac{30n^2+6}{10n^3+15n^2+11n+3}}$$

where N, N_s and n are total number of atoms, number of atoms in surface and the cluster order respectively.
Surface to volume ratio of a cubo-octahedral structure

$$\frac{N_s}{2N} = \frac{30n^2+6}{2(10n^3+15n^2+11n+3)}$$
$$\frac{N_s}{2N} = \frac{15n^2+3}{10n^3+15n^2+11n+3} \quad \ldots(4)$$

Cluster order n is given as

$$n = \frac{1}{2}\left[\left(\frac{r}{r_0}-1\right)\right]^2$$
$$\frac{N_s}{2N} = \frac{15\left(\frac{r}{r_0}\right)^2-30\left(\frac{r}{r_0}\right)+27}{\left(\frac{r}{r_0}\right)\left[5\left(\frac{r}{r_0}\right)^2+7\right]}$$

The surface to volume ratio of cubo-octahedral structure in terms of cluster diameter D is given as

$$\frac{N_s}{2N} = \frac{15\left(\frac{D}{d}-1\right)^2+12}{\left(\frac{D}{d}\right)\left[5\left(\frac{D}{d}\right)^2+7\right]} \quad \ldots(5)$$

The generalised expression for cohesive energy in terms of cubo-octahedral structure is given as

$$E_n = E_b\left[1-\gamma\left\{\frac{15\left(\frac{D}{d}-1\right)^2+12}{\left(\frac{D}{d}\right)\left[5\left(\frac{D}{d}\right)^2+7\right]}\right\}\right] \quad \ldots(6)$$

The cohesive energy and the melting temperature are parameters to estimate the strength of bonds in different aspects. It is reported that the cohesive energy has linear relation with the melting temperature for a material material (Rose, *et al*, 1982 and Guinea *et al*, 1984). The cohesive energy of a nanosolid is the function of N_s/N which depends on the size and shape of the nanomaterial, its melting temperature should follow a relation similar to cohesive energy

$$T_{mn} = T_{mb}\left(1-\frac{N_s}{2N}\right) \quad \ldots(7)$$

The generalized melting temperature for different shapes in terms of dimension factor γ is written as follows

$$T_{mn} = T_{mb}\left(1-\gamma\frac{N_s}{2N}\right) \quad \ldots(8)$$

The melting temperature of nanomaterials in terms of cubo-octahedral structure is presented as

$$T_{mn} = T_{mb}\left[1-\gamma\left\{\frac{15\left(\frac{D}{d}-1\right)^2+12}{\left(\frac{D}{d}\right)\left[5\left(\frac{D}{d}\right)^2+7\right]}\right\}\right] \quad \ldots(9)$$

where T_{mn} is the melting temperature of a nanomaterial and T_{mb} is the melting temperature of corresponding bulk material

Although, the values of melting temperature are different for different shapes so, we can generalise the above equation by inserting dimension factor γ for cubo-octahedral structure.

$$\boldsymbol{T_{mn} = T_{mb}\left[1 - \gamma\left\{\frac{15\left(\frac{D}{d}-1\right)^2+12}{\left(\frac{D}{d}\right)\left[5\left(\frac{D}{d}\right)^2+7\right]}\right\}\right]} \quad \ldots(10)$$

where γ is dimension factor, the value of γ is 1, 2/3, 1/3 for nanosolid, nanowire and nanofilm respectively (Vanithakumari and Nanda 2008). We use above equation for different shapes *i.e.* nanosolid, nanowire and nanofilm as follows

FOR NANOSOLID

For nanosolid we put $\gamma = 1$ (Guinea, *et al.*, 1984) then the Eq. (10) becomes

$$\boldsymbol{T_{mn} = T_{mb}\left[1 - \left\{\frac{15\left(\frac{D}{d}-1\right)^2+12}{\left(\frac{D}{d}\right)\left[5\left(\frac{D}{d}\right)^2+7\right]}\right\}\right]} \quad \ldots(11)$$

FOR NANOWIRE

For nanowire we put $\gamma = 2/3$ (Guinea, *et al.*, 1984) then the Eq. (10) becomes

$$\boldsymbol{T_{mn} = T_{mb}\left[1 - \frac{2}{3}\left\{\frac{15\left(\frac{D}{d}-1\right)^2+12}{\left(\frac{D}{d}\right)\left[5\left(\frac{D}{d}\right)^2+7\right]}\right\}\right]} \quad \ldots(12)$$

FOR NANOFILM

For nanofilm we put $\gamma = 1/3$ (Guinea, *et al.*, 1984) then the Eq. (10) becomes

$$\boldsymbol{T_{mn} = T_{mb}\left[1 - \frac{1}{3}\left\{\frac{15\left(\frac{D}{d}-1\right)^2+12}{\left(\frac{D}{d}\right)\left[5\left(\frac{D}{d}\right)^2+7\right]}\right\}\right]} \quad \ldots(13)$$

This is the mathematical expression for determining the melting temperature of the nanomaterials with different shapes as nanosolid, nanowire and nanofilm.

RESULT AND DISCUSSION

The expression for the size dependent melting temperature of nanomaterials in present work is derived from their cohesive energy. It should be mentioned that the present model for the size dependent cohesive energy is only for the free surface nanomaterials. Melting temperature is a parameter to estimate the strength of metallic bonds; hence its proportionality with cohesive energy is expectable. The scaling relation between the melting point of pure metals to their cohesive energy inferred from the universal binding theory of solids (Rose, *et al.*, 1982) is $T_{mn}(N) = 0.032\, E_c(N)/k_B$. This expression confirms a linear relation between melting point and cohesive energy for bulk materials. By applying this proportionality to the nanoscale, we have

$$\frac{\boldsymbol{E_n}}{\boldsymbol{E_b}} \approx \frac{\boldsymbol{T_{mn}}}{\boldsymbol{T_{mb}}}$$

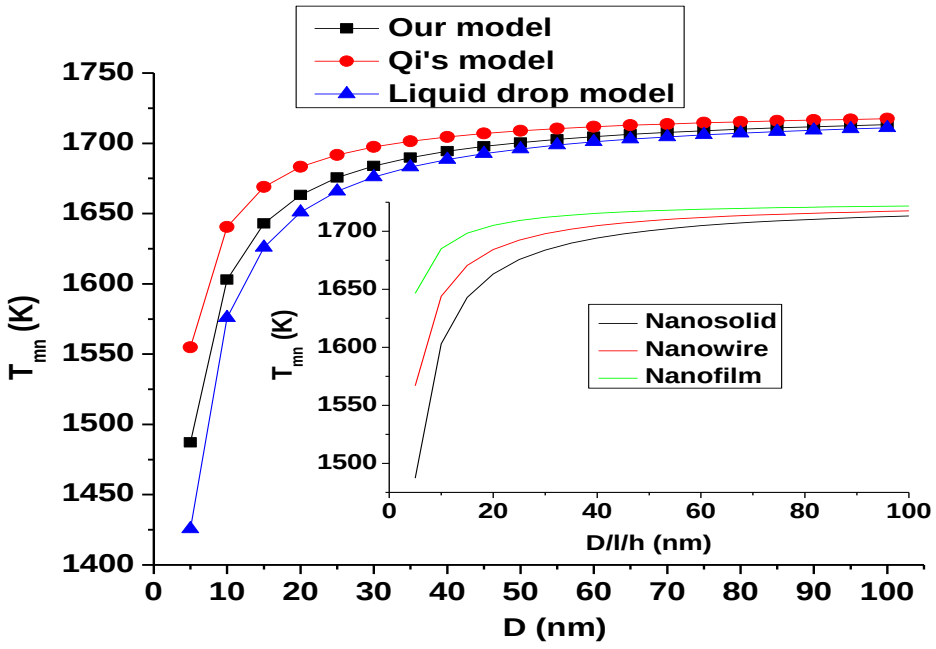
The melting temperature reduction of nanomaterial is apparent only when the cluster size is smaller than 100 nm. If the cluster size is larger than 100 nm, the melting temperature of the metals approximately equals to the corresponding bulk materials. If

the particle size is large enough (larger than 100 nm), the percentage of the surface atoms is fairly small. According to the present model, the variation of melting temperature of nanomaterials with cluster size is obtained due to the effect of surface atoms, but effect of surface atom on the melting temperature is negligible for bulk counterpart due to small percentage of surface atoms. If the cluster size is fairly large, we have $N_s \to \theta$ and $T_{mn} \approx T_{mb}$ in Eq. (11-13). All the necessary parameters for calculating the melting temperature of nanomaterials are listed in Table 1.

Table 1: Atomic diameters and bulk melting temperature of nanomaterials (Kittel 2005)

Nanomaterials	d (nm)	T_{mb} (K)
Ni	0.2480	1726.00
Pb	0.3870	600.06

The size and shape effects on the melting temperature of Ni nanomaterial have been shown in Graph 1 of T_{mn} *(D).* The comparisons are not given for nanosolid, nanowire, nanofilm because no experimental or MD simulation results are available for nanosolid, nanowire, nanofilm. It is clear from the inset of Graph 1 that the melting temperature of nanomaterials is different for different shapes and this Graph also justify the inclusion of γ. Although the values of γ are different for different shapes, our results of γ =1 for nanosolid, γ =2/3 for nanowire and γ =1/3 for nanofilm. So, the Graph demonstrate that the melting temperature have different value for different shapes. These facts also confirm the validity of Eqs. (11-13). In terms of Eqs. (11-13), T_{mn} *(D)* values are different for nanosolid, nanowire and nanofilm with the same *D* values. T_{mn} *(D)* of nanofilm is larger than that of nanowire and nanosolid due to γ < 1.

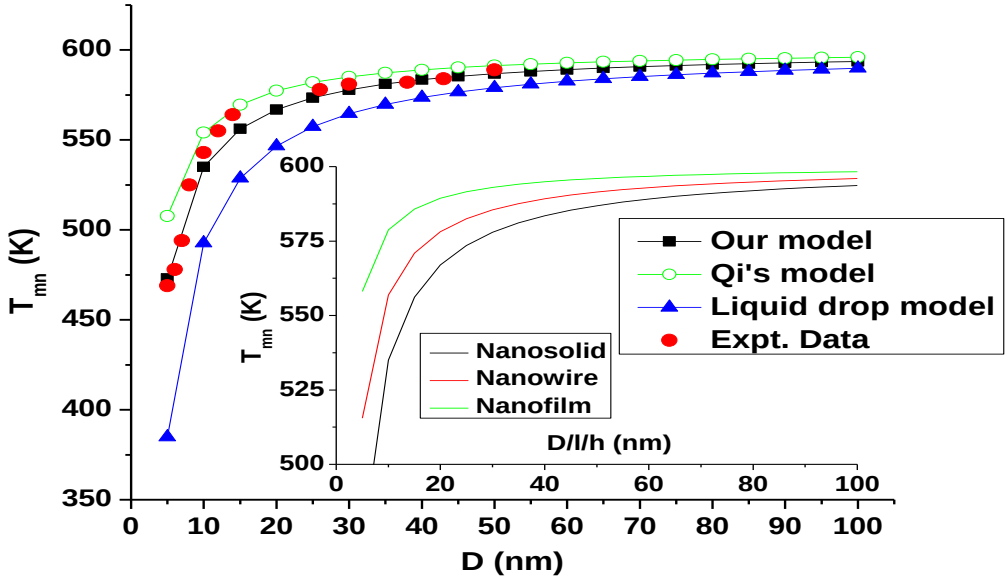


Graph 1: Melting temperature T_{mn} as the function of cluster size D of Ni nanomaterial

In Graph 1 the solid line with different symbol denotes the different model predications as mentioned in Graph. Inset Graph shows the melting temperature as the function of cluster size with different shapes of nanomaterial as Nanosolid, Nanowire and Nanofilm in terms of Eqs. (11-13) respectively.

Graph 2 shows the size and dimensionality effects on the melting temperature of Pb nanomaterials. It is found that T_{mn} *(D)* of Pb nanosolid decreases with reducing the cluster

size, and the drop of T_{mn} *(D)* becomes dramatic when *D* is below 20 nm. However, the sharp decrease happens at *D* < 20 nm for nanosolid as compared with nanowire and nanofilm. The trend of our model predictions is same with the other theoretical model results, as shown in Graph 2.



Graph 2: Melting temperature T_{mn} as the function of cluster size D of Pb nanomaterial

In Graph 2 the solid line with different symbol denotes the different model predications as mentioned in Graph. Inset Graph shows the melting temperature as the function of cluster size with different shapes of nanomaterial as Nanosolid, Nanowire and Nanofilm in terms of Eqs. (11-13) respectively (Jiang, et al., 1999).

The comparative study between our model predictions in terms of Eqs. (11-13) with Qi's model and Liquid drop model and the available experimental and simulation results for T_{mn} *(D)* functions of Ni, and Pb nanosolid, nanowire and nanofilm are shown in Figs. 1-2 respectively. From Figs., it is shown that the model predictions are well consistent with the experimental and simulation data, which illustrate the correctness of Eqs. (11-13). Although the fitted simulation T_{mn} values of these nanomaterials are slightly lower than the values of corresponding bulk materials. It is shown that the melting temperature of metallic nanoparticles decreases with decreasing the cluster size. The reduction of melting temperature is dramatic in the lower range of size, while it becomes smoothly in large size. When the cluster size is very small, the surface to volume atomic ratio increases, as the surface area increases. For a cluster size with diameter *D* = 20 nm, the surface atoms occupy ~45% of the total number of atoms and affect the melting temperature of the nanomaterials. For a cluster diameter of 100 and 1000 nm, the surface atoms are only 2.5% and 0.25% of the total number of atoms in the nanomaterial, respectively. Therefore, the surface effect becomes less impact on the melting temperature as the size increases.

CONCLUSION

The increasing or decreasing of melting temperature of nanometal depends on the surface of the nanomaterials, which means that the free surface results in the decreasing of the melting temperature and coherent interface may lead to the increasing of melting temperature with reduction of the cluster size. It is noticed that the melting temperature of the nanomaterials decreases with decreasing of the cluster size due to the creation of instability of the atoms. Nanofilms have higher melting temperature then the nanowires

and nanosolids at a particular cluster size due to the larger bond energy between the surface atoms and interior atoms in nanofilms. The results demonstrate that the variation of melting temperature is slant with cluster size above 20 nm while it is sharp with cluster size below 20 nm due to the presence of large surface atoms at D < 20 nm. Melting temperature is also depends on the dimension of nanomaterials i.e. lower the dimension of nanomaterials is diminishing the melting temperature.

Our results of cohesive energy and melting temperature are in good agreement with experimental and simulation data. The tendency of our study is similar to that of Qi's model (Qi 2005) and Liquid drop model (Nanda, *et al.*, 2002) Hence the present model of cohesive energy and melting temperature, which are based on quasi-spherical cluster shape, may have potential application in the research of thermo-elastic properties of the nanomaterials.

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