Effect of size on cohesive energy, melting temperature and Debye temperature of nanomaterials

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A simple model has been used to study the size dependence of cohesive energy, melting temperature and Debye temperature. We have considered W, Ag, Al, Co and Au for the study of size dependence of cohesive energy and Al, Au, Ag, Zn, Bi for size dependence of melting temperature. The results obtained are compared with the available experimental data. A good agreement between theory and experiment encouraged the authors to extend the model to study the size dependence of Debye temperature. The results obtained for the size dependence of the Debye temperature are found to be in good agreement with the experimental data. This supports the validity of the model developed.

Keyword: Elements, Nanostructures, Mechanical properties, Surface properties, Thermodynamic properties

1 Introduction

The material is considered to be nanomaterial if its average or crystalline size is less than 100 nm. The crystals of these sizes contain as few as a thousand atoms and have remarkable and potentially valuable characteristics. The properties vary with the size. These nanocrystals can emit light and are in sharp contrast to large structures. Quantum confinement resulting from their reduced dimensions causes to colour of light they emit to depend on their size. Since the nanostructured materials have a large number of surface atoms, therefore, surface energy becomes a very important property. Atoms on the surface of the solid have the greater energy than an atom in the interior. Compared with the bulk, nanosystems can have more rich metastable structures due to the surface effect.

Experimental study of size dependence of cohesive energy of W was carried out by Kim et al.\textsuperscript{2}, Xiao et al.\textsuperscript{3} as well as Hou et al.\textsuperscript{4} studied the size dependence of cohesive energy of Ag and Co nanoparticles using computer simulations. A theoretical study of size dependence of cohesive energy for Ag, Co, Al and Cu nanoparticles was carried out by Zhu et al.\textsuperscript{5}. The size dependence of melting temperature of nanocrystalline Au has been performed by Cottie.\textsuperscript{6} Wang et al.\textsuperscript{7} have studied the size dependence of melting behaviour of Zn nanowire using X-ray diffraction and transmission electron microscopy. Olson et al.\textsuperscript{8} studied the size dependence of melting temperature of Bi nanofilm. Sun et al.\textsuperscript{9} studied the size dependence of melting temperature of Al nanoparticles. Thus, it seems that there are experimental studies regarding the size dependence of the properties of nanomaterials. Moreover, the theoretical efforts are lacking. A hypothesis about the size dependence of cohesive energy and melting temperature has been reported by Qi\textsuperscript{10}. The model has been found quite satisfactory. Thus, it may be useful to extend this model to study size dependence of properties of nanomaterials viz. cohesive energy, melting temperature and Debye temperature which is the purpose of present work.

2 Theory

The cohesive energy ($E_{\text{Tot}}$) of the nanosolid is the sum of the contributions of the surface atoms and the interior atoms\textsuperscript{10}, which may be written as follows:

$$E_{\text{Tot}} = E_0 (n - N) + \frac{1}{2} E_0 N$$

where $E_0$ is the cohesive energy per atom, $n$ the total number of atoms of a nanosolid and $N$ is the number of surface atoms. Here surface atoms refer to the first layer of the nanosolid. Obviously, the number of interior atoms is $(n-N)$. Thus, Eq. (1) may be rewritten as:

$$E_n = E_b \left( 1 - \frac{N}{2n} \right)$$

where $E_n$ is the cohesive energy per mole of the nanosolid, which is given by:

-
\[ E_n = \frac{AE_{\text{Tot}}}{n} \quad \text{... (3)} \]

where \( A \) is the Avogadro constant and \( E_0 = AE_0 \).

It is well known that both the cohesive energy and the melting temperature are the parameters to describe the bond strength of materials. It has also been reported that the cohesive energy has the linear relation to the melting temperature of the material\(^{11,12}\). Following this concept Qi\(^{10}\) reported the following relation for the melting temperature:

\[ T_{mn} = T_{mb} \left( 1 - \frac{N}{2n} \right) \quad \text{... (4)} \]

where \( T_{mn} \) and \( T_{mb} \) are the melting temperature of nanosolid and corresponding bulk material, respectively. \( N/2n \) depends on the size and shape of the nanomaterials.

**Case (1): Spherical nanosolid**

For a spherical nanosolid with the diameter \( D \), its volume is \( \pi D^3/6 \). The atomic volume of the nanosolid can be written as \( \pi d^3/6 \), where \( d \) is the diameter of the atom. The total number \( n \) can be the volume ratio of nanosolid and the atom, i.e. \( n = (\pi D^3/6)/(\pi d^3/6) \), which gives \( n = D^3/d^3 \). The surface area of the nanosolid is \( \pi D^2 \), and the contribution of each surface atom to surface area of nanosolid is the area of the great circle of the atom, i.e. \( \pi d^2/4 \). The total surface atoms are the ratio between the surface area of nanosolid and the area of great circle of the atom, i.e. \( N = \pi D^2/(\pi d^2/4) \), which is simplified as \( (N/2n) = (2d/D) \). Therefore, Eqs (2 and 4) can be written as\(^{10}\):

\[ E_n = E_b \left( 1 - \frac{2d}{D} \right) \quad \text{... (5)} \]

and

\[ T_{mn} = T_{mb} \left( 1 - \frac{2d}{D} \right) \quad \text{... (6)} \]

**Case (2): Nanowire**

For nanowire with diameter \( L \) and height \( h \), the volume is \( \pi L^2h/4 \) and then total number of atoms \( n \) can be the volume ratio of nanosolid and the atom, i.e. \( n = 3L^2h/2d^3 \). The total surface area of nanosolid is \( (\pi L^2/2) + \pi Lh \), and the total surface atom is the ratio between the surface area of nanosolid and the area of the great circle of the atom, i.e. \( N = (2L^2 + 4Lh)/d^2 \). Therefore, Eq. (2) may be written as\(^{10}\):

\[ \frac{N}{2n} = \frac{2d}{3} \left( \frac{2}{L} + \frac{1}{h} \right) \quad \text{... (7)} \]

For nanowire \( h >> L \) and therefore, \( (N/2n) = (4d/3L) \). Thus, Eqs (2 and 4) can be written as follows:

\[ E_n = E_b \left( 1 - \frac{4d}{3L} \right) \quad \text{... (8)} \]

and

\[ T_{mn} = T_{mb} \left( 1 - \frac{4d}{3L} \right) \quad \text{... (9)} \]

**Case (3): Nanofilm**

In the case of nanofilm \( L >> h \), hence from Eq. (7), \( N/2n = (2d/3h) \). Thus, Eqs (2 and 4) give the following relation\(^{10}\):

\[ E_n = E_b \left( 1 - \frac{2d}{3h} \right) \quad \text{... (10)} \]

and

\[ T_{mn} = T_{mb} \left( 1 - \frac{2d}{3h} \right) \quad \text{... (11)} \]

The Lindemann criterion of melting, known to be valid for small particles, which states that a crystal melts when the root mean square displacement of atoms in the crystal exceeds a certain fraction of the interatomic distance\(^{11}\). Using this, the relationship between the melting temperature \( (T_m) \) and the Debye temperature \( (\theta_D) \) of the crystal can be written as follows\(^{12}\):

\[ \theta_D = \text{const} \left( \frac{T_m}{MV^{2/3}} \right)^{1/2} \quad \text{... (12)} \]

where \( M \) is the molecular mass and \( V \) is the volume per atom. Using Eq. (12), Liang and Baowen\(^{13}\) reported the following relation:

\[ \left( \frac{\theta_{Dn}}{\theta_{Db}} \right) = \left( \frac{T_{mn}}{T_{mb}} \right)^{1/2} \quad \text{... (13)} \]

where \( \theta_{Dn} \) is the Debye temperature of nanomaterial and \( \theta_{Db} \) the Debye temperature of corresponding bulk material. Combining Eqs (4 and 13), we get the following relation:

\[ \theta_{Dn} = \theta_{Db} \left( 1 - \frac{N}{2n} \right)^{1/2} \quad \text{... (14)} \]
Thus, for spherical case we can rewrite Eq.(14) as follows:

$$\theta_{Dn} = \theta_{D0} \left( 1 - \frac{2d}{D} \right)^{1/2} \quad \ldots \text{(15)}$$

Eq. (15) may be used to determine the size dependence of $\theta_{Dn}$.

3 Results and Discussion

Qi $^{10}$ used Eq. (4) to study the size dependence of melting temperature of Sn nanoparticle, Pb nanoparticle, In nanowire and nanofilm, a good agreement has been obtained with the experimental data. This encouraged the authors to extend the model. The values of cohesive energy have been calculated using Eq. (5) for spherical nanosolids. Input parameters required for the present work$^{2,5}$ are given in Table 1. The size dependence of cohesive energy of W nanocrystal using Eq.(5) is shown in Fig. 1. It is seen that the cohesive energy of W nanocrystal decreases on increasing the crystal size. The results obtained are compared with the available experimental data$^{2}$. There is reasonably good agreement between theory and experiment. The size dependence of cohesive energy of Ag nanoparticle using Eq. (5) is shown in Fig. 2. We compared our results with the experimental data$^{3}$ as well as reported by Zhu et al$^{5}$. It is observed that the trend of variation is same. Moreover, our results are slightly lower than the results obtained by Zhu et al$^{5}$, and agree with the experimental data$^{3}$. Size dependence of cohesive energy of Co nanoparticle is shown in Fig. 3 alongwith the experimental data$^{4}$ as well as reported by Zhu et al$^{5}$. The experimental data are available for very small range. Our results agree with these experimental data$^{4}$ and follow the trend as reported by Zhu et al$^{5}$. Size dependence of cohesive energy of Al and Cu nanoparticles is shown in Figs 4 and 5. For these materials, experimental data are not available. We compared our results with that reported by Zhu et al$^{5}$. For Al nanoparticle, our results are slightly lower than that reported by Zhu et al$^{5}$, up to the particle size 22 nm, and become higher when the particle size is further increased. For Cu nanoparticle, the results follow a similar trend of variation as reported by Zhu.

<table>
<thead>
<tr>
<th>Nanomaterial</th>
<th>$E_n$ (kJ/mol)</th>
<th>d (nm)</th>
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<tbody>
<tr>
<td>W</td>
<td>-924</td>
<td>0.3100</td>
</tr>
<tr>
<td>Ag</td>
<td>-295.9</td>
<td>0.2880</td>
</tr>
<tr>
<td>Co</td>
<td>-423.06</td>
<td>0.2500</td>
</tr>
<tr>
<td>Al</td>
<td>-321.87</td>
<td>0.2600</td>
</tr>
<tr>
<td>Cu</td>
<td>-337.29</td>
<td>0.2560</td>
</tr>
</tbody>
</table>

Table 1 — Values of input parameters [2, 5] for spherical case.
et al. It may be concluded that the cohesive energy of the nanoparticle decreases as the particle size increases for all the cases considered in the present study.

Size dependence of melting temperature of different nanomaterials computed using Eqs (6, 9, 11) is plotted in Figs 6-10. Input parameters required for this purpose are given in Table 2. The results of Au nanoparticle using Eq. (6) are shown in Fig. 6 along with the available experimental data. It is found that the results obtained are in good agreement with the experimental data. The melting temperature of Au nanoparticle increases on increasing the particle size up to 40 nm and is almost constant above 40 nm. Size dependence of melting temperature of Zn nanowire using Eq. (9) is shown in Fig. 7. The results obtained are compared with the experimental data. A good agreement is obtained. It is found that the melting temperature of Zn nanowire increases as the diameter of the nanowire increases. We studied the size dependence of melting temperature of Bi nanofilm using Eq. (10). The results obtained are
reported in Fig. 8 along with the experimental data. The trend of variation is similar to that of the experimental data. Moreover, our results are slightly low as compared with the experimental data.

The melting temperature of the Bi nanofilm increases up to film thickness 10 nm and then seems to become constant. Size dependence of melting temperature of Al nanoparticle computed using Eq. (6) is shown in Fig. 9. The results obtained are compared with the experimental data. There is a good agreement between theory and experimental data for \(D > 40\) nm. It is found that the melting temperature of Al nanoparticle increases as particle size increases up to 100 nm. We have also studied the size dependence of melting temperature of Ag nanoparticle using Eq. (6). The results obtained are shown in Fig. 10. It is found that the melting temperature increases with increasing the particle size.

A good agreement between theory and experiment encouraged the authors to extend the model for the study of size dependence of Debye temperature. The model gives Eq. (15) for the size dependence of \(\theta_D\n\).
We used this relation to compute size dependence of Au, Se and $\beta$-Sn. The input parameters required are given in Table 3. The computed values of $\theta_{Dn}$ for Au, Se and $\beta$-Sn are given in Figs 11-13 alongwith the experimental data\textsuperscript{14}. There is a good agreement between theory and the experiment for all the materials considered in the present work. This demonstrates the suitability of the model presented for $\theta_{Dn}$.

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**References**