Size dependent Debye temperature and mean square displacements of nanocrystalline Au, Ag and Al

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ARTICLE INFO
Article history:
Received 29 July 2008
Received in revised form 19 December 2008
Accepted 8 February 2009

Keywords:
Nanocrystalline Au, Ag and Al
Melting point
Liquid drop model
Lattice contraction
Debye temperature and mean square displacement

ABSTRACT
In the present work the size dependent Debye Temperature (θD) and Mean Square Displacements (MSDs) of nanocrystalline Au, Ag and Al are determined. Size dependent melting temperature (Tm) of these nanoparticles is determined by the expression derived by Nanda et al. following liquid drop model. The size dependent lattice contraction is properly accounted following Qi and Wang. The Debye temperatures are determined from the values of melting temperatures by Lindemann theory of melting. The calculated values of relative Debye temperature change for nanophase Au are agreeing well with the experiments. The procedure is extended to determine the MSDs of Au, Ag and Al for sizes ranging from 2 nm to 50 nm at 300 K. The results show that the size effect on θD and MSDs are predominant in the sizes ranging from 2 nm to 10 nm.

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1. Introduction

The study of nanocrystalline materials is an active area of research in physics, chemistry and materials sciences [1,2]. While numerous techniques are known to produce nanostructures, it is much more difficult to determine the properties of such small collections of atoms. Different physical properties such as mechanical strength, plasticity, melting, sintering and alloying ability, diffusivity, chemical reactivity and the mode of crystal growth have been found depend upon particle size. Size dependent melting point depression of small particles has been studied for many years both theoretically and experimentally [3]. The technical advantages of the low melting temperatures of small particles are (i) the ability to fuse nanoparticles to form a film at a relatively low temperature, (ii) possibility of soldering at relatively low temperatures using nanoparticles, (iii) possibility of controlling the growth process of nanoparticles by controlling the deposition or substrate temperature.

The Debye Temperature (θD) of nanocrystals is an essential physical quantity to characterize many material properties such as thermal vibrations of atoms and phase transitions. Also the Einstein temperature and volume expansion coefficient are related with θD. Hence, if the size effect on θD is known, the size effect on other related properties can be easily determined. As experimental and theoretical investigations in this direction are very less, it is planned to determine the size effect on the Debye Temperature (θD) and Mean Square Displacements (MSDs) of nanocrystalline Au, Ag and Al.

Melting temperature (Tm) of nanogold with particle sizes in the range 20–50 Å is studied experimentally and theoretically by Buffat and Borel [4]. They proposed a phenomenological model to determine the melting temperature of particles with different sizes. Also Jiang, et. al [5] introduced a simple model, free of any adjustable parameter, for the size dependent melting of nanocrystals. Recently Nanda et. al. [6] derived an expression for the size dependent melting of low dimensional systems following the liquid drop model [7]. Although the results from [4,5,6] are in good agreement with experiments they have not properly accounted the size dependent lattice contraction. In the present work the melting temperatures of Au, Ag and Al nanoparticles are determined from liquid drop model proposed by Nanda et. al [6] by properly accounting the size dependent lattice contraction. From the calculated values of melting temperatures, the size dependent Debye temperatures and MSDs are determined by the Lindemann theory [8].

2. Liquid drop model for size dependent melting

One of the successes of the liquid drop model lies in providing an intuitive explanation for the phenomenon of spontaneous fission of some nuclei. Atomic clusters and nanoparticles being finite systems, their properties are dominated by the surface atoms, therefore their binding energy can be effectively represented by the volume and surface dependent term as in the liquid drop model. From this point of view the melting of atomic clusters and nanoparticles...
can be understood by scaling the cohesive energy to the melting temperature. Based on the liquid drop model [7], Nanda et al. [6] derived an empirical relation for the size dependent melting temperature of nanoparticles (T_{mb}) in terms of bulk melting temperature (T_{mb}) as,

\[ T_{mb} = T_{mb} - \frac{6\sigma v_o}{0.0005736d} \]

where \( v_o \) is the molar volume, \( d \) is the diameter of the particle and \( \gamma \) represents the coefficient of surface energy of the material. Here the particle shape is assumed to be spherical. For a nanomaterial with general shape, the size dependent melting, in general, can be written as

\[ T_{mb} = T_{mb} - \frac{\beta}{d} \]

with \( z = 1, 3/2, \) and 3 for nanoparticles, nanowires, and thin films. In Eq. (3), \( d \) represents the diameter in case of nanoparticles and nanowires, whereas it represents the thickness in case of thin films.

Similar expressions for size dependent melting for spherical nanoparticles has also been derived from thermodynamic arguments [4,9] and from a model based on surface phonon instability [10]. Using the known values of \( v_o, \gamma \) and \( T_{mb} \), the values of \( \beta \) for different elements are estimated by Nanda et al. [6] and are tabulated in Table 1. Nanda et al. [6] compared their results with the theoretical predictions of Jiang et al. [11] and found that both the models [6,11] are consistent for Pb thin films.

### Table 1

<table>
<thead>
<tr>
<th>Element</th>
<th>( \gamma ) [J/m(^2)] at 298 K</th>
<th>( T_{mb} ) K</th>
<th>( v_o \times 10^{-6} \text{ m}^3 )</th>
<th>( \beta ) nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au</td>
<td>1.508</td>
<td>1337.6</td>
<td>10.21</td>
<td>1.1281</td>
</tr>
<tr>
<td>Ag</td>
<td>1.205</td>
<td>1234</td>
<td>10.27</td>
<td>0.9656</td>
</tr>
<tr>
<td>Al</td>
<td>1.146</td>
<td>931.25</td>
<td>10.00</td>
<td>1.2</td>
</tr>
</tbody>
</table>

3. **Size dependent lattice parameters**

It is proved experimentally and theoretically that the lattice parameters of nanoparticles depend on the particle size [12-16]. For an isolated nanoparticle, the lattice constants are often measured to contract. Montano et al. [17] measured the nearest neighbour distance of isolated silver particles with sizes from 2.5 nm to 13 nm and found a noticeable contraction in the nearest neighbour distance. Also, the model developed by Jiang et al. [18,19] based on the Laplace–Young equation supports the size induced lattice contraction. Recently Qi and Wang [20] developed a simple model to account for the size and shape dependent lattice parameters of metallic nanoparticles. They have assumed that a nanoparticle is formed in the three steps. First a particle is taken out from an ideal bulk crystal without changing structure, for the formation of nanoparticle, one can imagine that a nanoparticle can have the same structure as that of its bulk counter part. Also the contraction in the lattice constant will lead to the change in molar volume of the nanoparticle. Hence from the corrected values of lattice constants obtained from Eq. (4), new molar volumes are determined for sizes ranging from 2 nm to 50 nm. Eq. 1 shows the volume contraction for Au, Ag and Al with respect to the reciprocal of the particle size. From Fig. 1 it can be seen that the volume contraction is appreciable in the sizes ranging from 2 nm to 10 nm. Obviously, we can expect that this volume contraction for small sizes can reflect in the determination of melting temperatures. Hence size dependent melting temperatures for Au, Ag and Al are determined from Eq. (1), by incorporating the volume contraction. The values of size dependent melting temperatures for Au obtained by our calculations are shown in Fig. 2 along with experimental results [4] and the results from liquid drop model [6]. Fig. 2 clearly explains that the results are very much improved when we consider the lattice contraction for determining the melting temperature of small sized particles.

### 4. Size dependent melting temperature considering lattice contraction

In the present work, the size dependent lattice constants for Au, Ag and Al were determined by Eq. (4). As the model proposed by Qi and Wang [20] assumes that a particle is taken from a bulk crystal without changing the structure, for the formation of nanoparticle, one can imagine that a nanoparticle can have the same structure as that of its bulk counter part. Also the contraction in the lattice constant will lead to the change in molar volume of the nanoparticle. Hence from the corrected values of lattice constants obtained from Eq. (4), new molar volumes are determined for sizes ranging from 2 nm to 50 nm. Fig. 1 shows the volume contraction for Au, Ag and Al with respect to the reciprocal of the particle size. From Fig. 1 it can be seen that the volume contraction is appreciable in the sizes ranging from 2 nm to 10 nm. Obviously, we can expect that this volume contraction for small sizes can reflect in the determination of melting temperatures. Hence size dependent melting temperatures for Au, Ag and Al are determined from Eq. (1), by incorporating the volume contraction. The values of size dependent melting temperatures for Au obtained by our calculations are shown in Fig. 2 along with experimental results [4] and the results from liquid drop model [6]. Fig. 2 clearly explains that the results are very much improved when we consider the lattice contraction for determining the melting temperature of small sized particles.

### 5. Debye temperature and mean square displacements

The forces between the atoms are reflected in the Debye temperature and it is useful to have this as a reference to characterise a crystal. The Debye temperature is a measure of the vibrational response of the material and therefore intimately connected with properties like the specific heat, thermal expansion and vibrational entropy [25]. Lighter inert gas solids melt below their \( \theta_D \) while the other crystals remain solids above it. The first theory explaining the

![Fig. 1. Percentage of molar volume contraction with respect to size. It can be seen that the volume change is appreciable for sizes from 2 nm to 10 nm.](image-url)
mechanism of melting in the bulk was proposed by Lindemann [8], who used vibration of atoms in the crystal to explain the melting transition. The average amplitude of thermal vibrations increases when the temperature of the solid increases. At some point the amplitude of vibration becomes so large that the atoms start to invade the space of their nearest neighbours and disturb them and the melting process initiates. Quantitative calculations based on the model are not easy, hence Lindemann offered a simple criterion that the melting might be expected when the root mean square displacement exceeds a certain threshold value (namely when the amplitude reaches at least 10% of the nearest neighbour distance). Although experiments confirm that the Lindemann criterion is not very accurate, it lends strong support to the idea that the magnitude of vibrational amplitude dominates the phenomenon of melting. Also Lindemann model for vibrational melting is adequate for simplest structures i.e. assemblies of closed packed atoms. Further, there are some discrepancies regarding the $T_m$ dependence of $\theta_D$. One opinion is that $\theta_D$ varies linearly with $T_m$ [26] and the other suggests a square root dependence of $\theta_D$ on $T_m$ according to Lindemann Criterion of melting [8]. Since there are more supporting evidences for the square root dependence [11], the size dependent $\theta_D$ and MSDs are determined by the Lindemann theory.

Following Lindemann theory, Reisland [27] derived the expressions for the Debye temperature and mean square displacement for a bulk crystal as

$$\theta_D = \theta_{D,\text{Lind}} \left( \frac{T_m}{m \theta_D^2} \right)^{1/2}$$

$$\langle u^2 \rangle = \frac{9 \hbar^2 T}{m k_B \theta_D^2}$$

where $m$ is the atomic mass and $\theta_{D,\text{Lind}}$ is the Lindemann constant and is equal to 200 for nonmetals and 137 for metals. $T$ is the temperature at which the MSDs are calculated.

Studies on the lattice structure of nanocrystalline samples by means of XRD and Massbauer spectroscopy showed that the lattice structure of the nanometer sized crystallites deviates from the equilibrium state. The deviation may be classified as (i) distorted lattice structures in pure elements and stoichiometric line compounds, and (ii) formation of metastable phase below a critical crystalline size. The lattice distortion in various nanocrystalline materials is manifested by a significant change in lattice parameter [28] and corresponding change in molar volume. Hence the expression for $\theta_D$ of a bulk crystal can be used for a nanocrystalline material by substituting the size dependent molar volume and melting temperature.

Determination of size dependent $\theta_D$ from specific heat measurements by Herr et al. [29] showed that $\theta_D$ decreases significantly for nanocrystalline materials. The depressed Debye temperature in nanocrystalline sample implies a decrease in the cohesion of atoms in the nanocrystallites, which agrees well with the measured grain size dependence of lattice parameter [30].

In the present work the size dependent Debye temperatures are determined from Eq. (6) by substituting the newly calculated melting temperatures and the size dependent MSDs are determined from Eq. (7) for Au, Ag and Al. Fig. 3 shows the size dependent relative change in Debye temperature for Au along with experimental results of Balerna and Mobilio [31]. Since the results are agreeing with experiments the size dependent Debye temperatures are determined for Ag and Al. Fig. 4 shows the size dependent Debye temperatures for Au, Ag and Al. It clearly explains that the $\theta_D$ values for Au, Ag and Al are decreasing with size, which is in agreement with the predictions of Herr et al. [29]. Fig. 5 shows the size effect on the MSDs for Au, Ag and Al at 300K. It shows that the values of MSDs are increasing along with reduction in sizes. Also from Figs. 4 and 5 it can be seen that the $\theta_D$ values are decreasing with respect to the decrease in size of the particle and the reduction is appreciable for sizes from 2 nm to 10 nm.
Table 2
Shear Modulus (G), Bulk Debye Temperature ($\theta_D$) and MSDs at 300K.

<table>
<thead>
<tr>
<th>Element</th>
<th>$G \times 10^{10}$ Nm$^{-2}$ [20]</th>
<th>$\theta_D$ (K)</th>
<th>Bulk MSD $\times 10^{-2}$ Å$^2$ [32]</th>
<th>MSD for 50 nm $\times 10^{-2}$ Å$^2$ [Present work]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au</td>
<td>2.60</td>
<td>170</td>
<td>2.40</td>
<td>2.52</td>
</tr>
<tr>
<td>Ag</td>
<td>3.03</td>
<td>215</td>
<td>2.85</td>
<td>2.73</td>
</tr>
<tr>
<td>Al</td>
<td>2.62</td>
<td>394</td>
<td>–</td>
<td>3.56</td>
</tr>
</tbody>
</table>

Fig. 5. Size effect on MSDs of Au, Ag and Al at 300K. The MSD values are increasing with respect to reduction in size. For aluminium the value of root mean square displacement is calculated as 7.38 percentage of nearest neighbour distance.

it can be seen that the size effect on $\theta_D$ and MSDs are predominant in the sizes ranging from 2 nm to 10 nm. When the size is above 20 nm the changes are too small to be neglected. The calculated values of MSDs for Au and Ag with size 50 nm at 300K are tabulated in Table 2. Available experimental values of MSDs for bulk Au and Ag [32] are shown for comparison.

6. Conclusion
The size effects on $\theta_D$ and MSDs for Au, Ag and Al are determined by considering the lattice contraction with size. The melting temperatures are determined by liquid drop model and $\theta_D$ and MSDs are determined from Lindemann theory. The calculated values of $\theta_D$ are agreeing well with experimental predictions. The present work suggests a simplest successful method for the determination of size effect on $\theta_D$ and MSDs.

Acknowledgement
The author wishes to acknowledge the management of Dr. Sivanthi Aditanar College of Engineering, Tiruchendur for constant encouragement.

References