Low Temperature Specific Heat Capacity of Au Nano-Particles with Their Size

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Abstract:
The present work deals with the specific heat capacity of Au nano-particles with their size at low temperature. Starting with the Lindemann's melting criterion, an expression for specific heat capacity at low temperature for nano-materials has been derived which illustrates the size dependency of specific heat capacity of Au spherical shape. It is observed that at low temperature, the specific heat capacity of Au nano-particles decreases with increase in their size.

Keywords- *Specific heat capacity, low temperature, nano-particles*

INTRODUCTION

Nano-materials (or nano-crystalline materials) are materials possessing grain sizes on the order of a billionth of a meter. They manifest extremely fascinating and useful properties which can be exploited for a variety of structural and non-structural applications. All materials are composed of grains which in turn comprise many atoms. These grains are usually invisible to the naked eye depending on their size. A nano-crystalline material has grains of the order of 1-100 nm [1].

Physical properties of nano-materials are related to different origins such as large fraction of surface atoms, large surface energy, spatial confinement, reduced imperfections. Large fraction of surface atoms means surface atoms have a much greater effect on chemical and physical properties of a nano-particle. The properties of nanoscale materials are influenced by size, shape, structure and orientation [2]. In materials where strong chemical bonding is present, delocalization of valence electrons can be extensive. The extent of delocalization can vary with the size of the system. The structure also changes with size. These two changes can lead to different physical and chemical properties depending on size such as specific heat capacity. The specific heat capacity of nano-materials plays an important role in their thermal behaviour. A very work has been done in this direction. However, there are some experimental and theoretical studies on specific heat of nano-materials.

The specific heat of Ag nano-particles at constant pressure has been measured considering the particles with surface atoms and inner atoms [3]. The specific heat of Cu nano-particles with their size has been studied theoretically [4]. A decrease in specific heat with increase in particle size has been observed. Very recently, the effect of size and shape on the specific heat of some nano-materials has been studied. A simple theory has been proposed to study the size and shape dependent specific heat of nano-materials. An increase in specific heat with the decrease in particle size has been observed.

The sufficient study of specific heat capacity with particle size at low temperature is still lacking which is very important. We, therefore, have planned to study the low temperature specific heat capacity of nano-materials with their size. In the present work, we have studied the low temperature specific heat capacity of spherical Au nano-particles with their size.

METHOD OF ANALYSIS

According to the Lindemann's melting criterion, a crystal melts when the root mean square displacement of atoms exceeds a certain fraction of the inter-atomic distance in the crystal. This criterion is valid for small particles. Using this theory, the relationship between the melting temperature and Debye temperature of the bulk material can be given as [6]-

$$\theta_{Db} = \text{Constant}\left(\frac{T_{mb}}{MV^{\frac{2}{3}}}\right)^{\frac{1}{2}} \tag{1}$$

Where M, V, T_m and θ_D are molecular mass, volume per atom, melting temperature and Debye temperature of the crystal respectively.

Similarly, for nano-materials, the above expression can be written as-

$$\theta_{Dn} = \text{Constant}\left(\frac{T_{mn}}{MV^{\frac{2}{3}}}\right)^{\frac{1}{2}} \tag{2}$$

From equations (1) and (2), we have the following correlations-

$$\frac{\theta_{Dn}}{\theta_{Db}} = \left(\frac{T_{mn}}{T_{mb}}\right)^{\frac{1}{2}} \qquad (3)$$

Here θ_{Dn} and θ_{Db} are Debye temperature of nano-material and that of corresponding bulk material respectively.
The relation for melting temperature of nano-material can be written as [5]-

$$\frac{T_{mn}}{T_{mb}} = \left(1 - \frac{N}{2n}\right) \qquad (4)$$

Where T_{mn} and T_{mb} are the melting temperature of nanosolid and that of corresponding bulk material respectively. Here N is the total number of surface atoms while n is the total number of atoms of a nanosolid.
Therefore, from equations (3) and (4), we have-

$$\frac{\theta_{Dn}}{\theta_{Db}} = \left(1 - \frac{N}{2n}\right)^{\frac{1}{2}} \qquad (5)$$

At low temperature, the specific heat capacity is given as [6]-

$$C_{vb} = \frac{12\pi^4 R}{5}\left(\frac{T}{\theta_{Db}}\right)^3 \qquad (6)$$

Where R is the ideal gas constant and T, the absolute temperature of the material.
Obviously,

$$C_{vb} \propto \left(\frac{T}{\theta_{Db}}\right)^3 \qquad (7)$$

For nano-particles, we can write-

$$C_{vn} \propto \left(\frac{T}{\theta_{Dn}}\right)^3 \qquad (8)$$

Thus, from (7) and (8), we get-

$$\frac{C_{vb}}{C_{vn}} = \left(\frac{\theta_{Dn}}{\theta_{Db}}\right)^3 \qquad (9)$$

From, equations (5) and (9), we get-

$$\frac{C_{vn}}{C_{vb}} = \left(1 - \frac{N}{2n}\right)^{-\frac{3}{2}} \qquad (10)$$

But for spherical nanosolid, we have [7]-

$$\frac{N}{n} = \frac{4d}{D} \qquad (11)$$

Where d and D are the diameter of an atom and diameter of the spherical nanosolid.
Therefore, the above expression (10) becomes-

$$\frac{C_{vn}}{C_{vb}} = \left(1 - \frac{2d}{D}\right)^{-\frac{3}{2}} \qquad (12)$$

This is the expression for low temperature specific heat capacity of nano-particles with their size.
For Au nano-particles, d = 0.228 nm [5,7,8], therefore the above relation becomes-

$$\frac{C_{vn}}{C_{vb}} = \left(1 - \frac{0.456}{D}\right)^{-\frac{3}{2}} \qquad (13)$$

The above expression can be used to study the low temperature specific heat capacity of spherical Au nano-particles with their size.

RESULTS AND DISCUSSION

The equation (13) has been used to compute the value of relative low temperature specific heat capacity of nano-particle ($\frac{C_{vn}}{C_{vb}}$) with their size (D). Figure (1) shows the variation of low temperature specific heat capacity $\frac{C_{vn}}{C_{vb}}$ of spherical Au nano-particles with their size. It is obvious from the graph that the low temperature specific heat capacity decreases with increase in particle size i.e. the specific heat capacity varies inversely with the particle size. The reason of the increased specific heat at small sizes is the high atomic thermal vibration energies of the surface atoms.

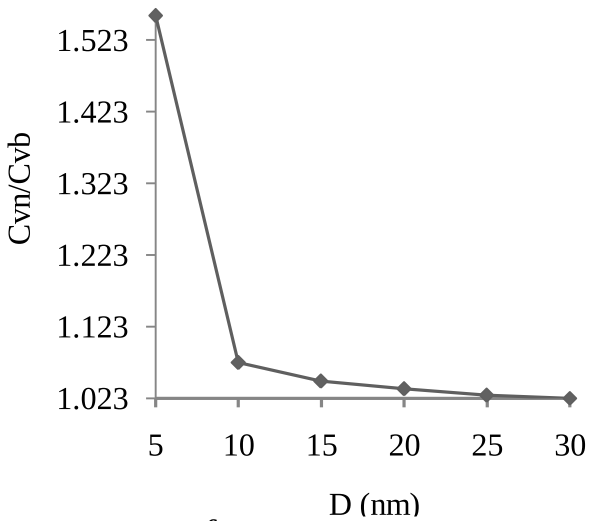

Figure 1: Variation of $\frac{C_{vn}}{C_{vb}}$ with particle size (D) at low temperature

CONCLUSION

In the present work, the low temperature specific heat capacity of spherical Au nano-particles with their size has been studied. The study shows a decrease in low temperature specific heat capacity with particle size i.e. the specific heat capacity varies inversely with the particle size.

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