

Short Communication

Influence of Size on the Melting Temperature of Metallic Nanoparticle

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Abstract

In This paper, the effect of size on melting temperature of metallic nanoparticles (Au, Pb and Bi) is theoretically simulated and explained. In this regard, the cause of difference in various experimental data is introduced, which is the difference between nanoparticles' grain Gaussian distribution. This volume-dependent model with the help of the Gaussian distribution can describe the relation between nanoparticle melting temperature and its size. The obtained results are interestingly consistent with reported experimental data.

Keywords: Melting Temperature, Nanoparticles, Distribution Function.

1. INTRODUCTION

A Melting point is one of the important thermodynamic properties of all materials. Nanoparticles with different sizes have different melting temperature which refers to the phenomenon of reduction in melting point of particles in small dimension. This phenomenon is interesting in nanoscale particles; for example, the decrease in melting temperature of metals with nanometer dimensions can be on the order of tens to hundreds of Kelvin degrees. The dependence of nanoparticles melting point on their size was first theoretically predicted by Pawlow in 1909 [1], and then was demonstrated by Takagi in 1954 [2]. There are several models that can describe the variation of melting temperature [3-8].

The high surface to volume ratio of nanoparticles leads to great effect of surface atoms on chemical and physical properties. In solids, because of fewer neighboring atoms, the cohesive energy of surface atoms is less than inner atoms in the bulk [9]. Gibbs-Thomson model is one of the most creditable models to appoint melting temperature of nanoparticles. This model is based on the changes of melting temperature at the surface atoms of nanoparticles. But for nanoparticles which have high heat conduction and dimensions between 20-100 nm, the effect of volume will be very important, consequently this model is not efficient in these case so a

model must be introduced to show the effect of volume on melting temperature.

2. MODEL

According to the numerical calculation of phonon spectrum for metallic nanoparticles [10], the surface layer atoms can be excited by lower frequencies. Hence, these atoms need lower temperature (T_p) for melting process. Since our model is based on spherical model and, for small spherical nanoparticles the melting process begins from the surface layer with δ thickness and ends to the central core of nanoparticles, we consider two spheres with r and $r-\delta$ radii (Fig. 1).

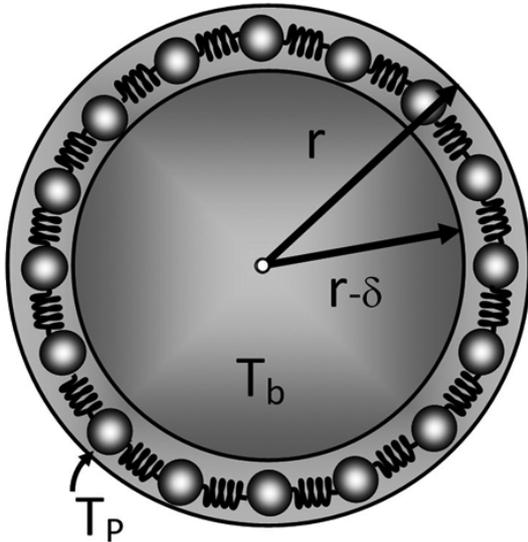


Figure 1. A nanoparticle with the solid core and a liquid shell.

Hence, the gradient of temperature, ΔT , is directed to the center of the inner core and is proportional to the change of the volume of nanoparticle (ΔV) as follows:

$$\frac{\Delta T}{T_b} = \alpha \frac{\Delta V}{V_{inner}} \quad (1)$$

Where $\Delta V = (V_{outer} - V_{inner}) = V_{shell}$ is the change in volume, $\Delta T = T_b - T_p$ is the change in temperature of the shell and, α and T_b are the constant coefficient and melting temperature of inner bulk core, respectively

(Figure 1). The coefficient α in Eq. 1 is a proportional coefficient which depends on the type of nanoparticle. It can be related to the atomic mass, electronic structure and inter atomic distance. So, it is changed by change of type of nanoparticle. But in this paper, dependence of α on effective parameters is not investigated and it is used only as the fitting parameter. The paper focuses on behavior of nanoparticle melting temperature variations by size. By replacing the ΔT and ΔV in Eq. 1, the next expression is obtained:

$$1 - \frac{T_p}{T_b} = \alpha \left(\frac{V_{outer}}{V_{inner}} - 1 \right) \quad (2)$$

Also, according to the Figure 1, we have:

$$\begin{cases} V_{outer} = \frac{4}{3} \pi r^3 \\ V_{inner} = \frac{4}{3} \pi (r-\delta)^3 \end{cases} \quad (3)$$

So, one can found the next equation:

$$\frac{T_p}{T_b} = 1 + \alpha \left[1 - \left(\frac{1 - \frac{\delta}{r}}{1 - \frac{\delta}{r}} \right)^3 \right] \quad (4)$$

Where δ is the thickness of the shell or the outer layer of the nanoparticle which is equal to atomic radius of atoms in nanoparticle. Therefore the melting temperature of a nanoparticle is a function of its curvature radius, and larger nanoparticles melt at greater temperatures. This equation can be verified for high limit: If r grows dramatically and tends to infinity ($r \rightarrow \infty$), bulk and particle (shell) melting temperature will be approximately the same which express that for large particles or bulk materials T_p is approximately the same as T_b .

$$\lim_{r \rightarrow \infty} \left(\frac{T_p}{T_b} \right) \rightarrow 1 \quad (5)$$

2.1. Distribution Function of Transition Temperature

In real nanomaterials, the nanoparticles are usually distributed with different sizes. The form and parameters of the distribution function depend on the technology of the sample production. We suppose that the distribution function of radius, r , has Gaussian form [11], namely

$$f(r, T) = A \exp \left[-\beta T \left(\frac{r - r_0}{2\sigma} \right)^2 \right], \quad 0 \leq r \leq \infty \quad (6)$$

where A, β, r_0 and σ are respectively normalization constant, the separation coefficient, the most probable radius of nanoparticles and standard deviation, respectively.

3. RESULTS AND DISCUSSIONS

The experimental data [12-18] and the results of our theoretical model for spherical metallic nanoparticles are plotted in the Figure 2 by using the Eqs. 4, 6 for gold (Au), lead (Pb) and bismuth (Bi). Figure 2 clearly shows a decrease in melting temperature with decrease of size. The obtained results from the theory are supported by reported experimental data.

The results are discussed and interpreted as follows: when the size of the nanoparticle is reduced, the ratio of number atoms in surface to number of atoms in volume is decreased. Therefore, the binding energy of surface atoms is reduced which causes the surface atoms are detached from nanoparticle by receiving of less energy.

Consequently, the melting temperature of the nanoparticle is reduced by decreasing of its size. But, after a certain value, when the nanoparticle size is increased, the ratio of number atoms in surface to number of atoms in volume tends to zero. So, the melting temperature goes up and is saturated.

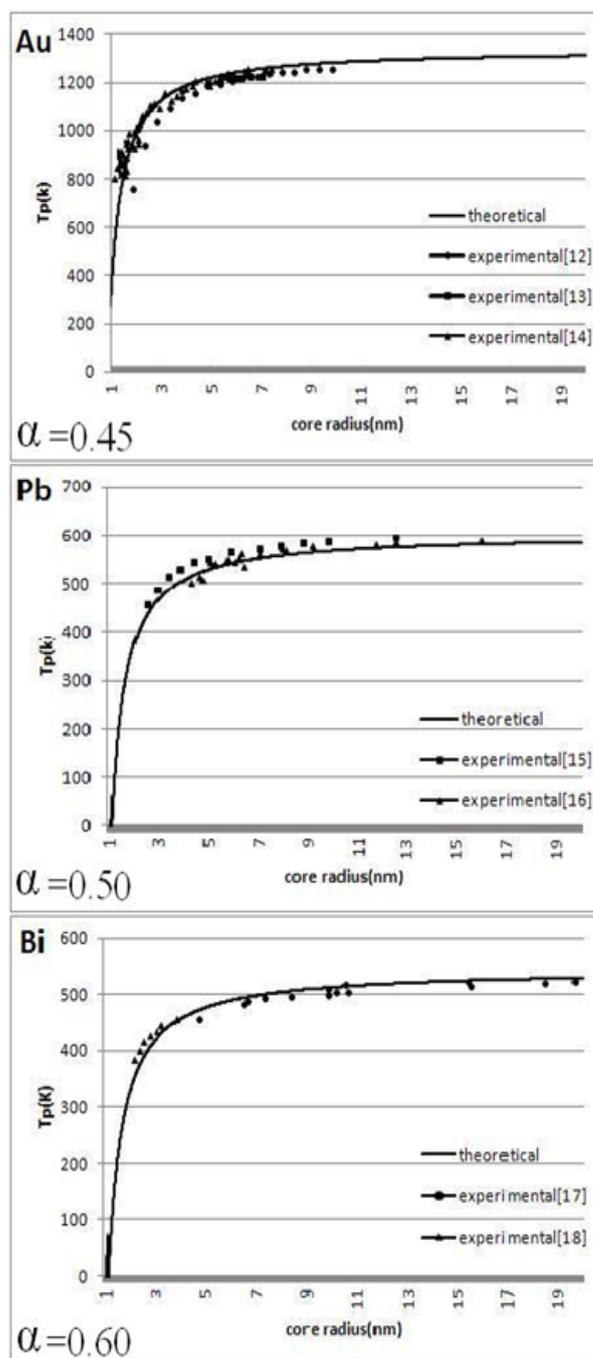


Figure 2. Melting temperature of Au, Pb and Bi nanoparticles as a function of radius. Solid curves are theoretical model results. Symbols are experimental data [12-18].

By using these curves, the coefficient, α , can be found experimentally. The values of α are registered in Table 1.

Table 1. The obtained coefficient α for different metallic nanoparticles.

Element	Melting point T_{bulk} [K]	Atomic radius r [nm]	coefficient α
Au	1337.33	0.144	0.45
pb	600.61	0.175	0.50
Bi	544.52	0.154	0.60

The 3D curve of $f(r, T)$ is drawn for gold nanoparticles in Figure 3. This figure shows that the melting temperature of the nanoparticles has the most distribution in the most available radii.

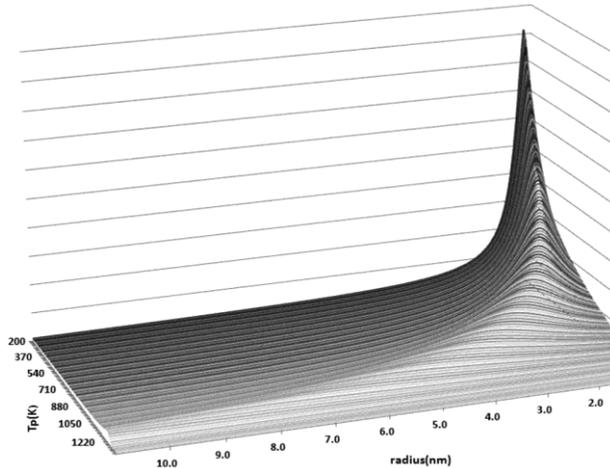


Figure 3. Distribution function of melting temperature for Au nanoparticles ($\beta = 0.0001$).

The dispersion of various experimental data in Figure 2 may be caused by the following factors:

- 1- In real products, the Gaussian distribution of nanoparticles is not symmetric.
- 2- The melting method.
- 3- The real shape of nanoparticles.
- 4- When the size decreases, the density of phonon modes gets irregular.

3- CONCLUSION

In this paper, it was shown that the melting temperature of metallic nanoparticles depends on volume changes. So a theoretical model was presented to describe the melting temperature of nanoparticles. In addition, we applied our theory to some metallic nanoparticle such as Au, Pb and Bi. Obtained values for coefficient α in the theory show that it can depend on heat capacity and atomic number of atoms in nanoparticle. The obtained results from the theory were in good agreement with experimental data.

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