

Size-dependent melting point of noble metals

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Abstract

A simple model, without any free parameter, is introduced to predict the size-dependent melting temperature of noble metals in this contribution. It is found that the model predictions for the melting point depression of both Au and Ag nanoparticles correspond to the experimental and computer simulation results well.

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1. Introduction

The physical properties of nanoparticles are a subject of intense contemporary interest [1]. As the size of low-dimensional materials decreases to nanometer size range, electronic, magnetic, optic, catalytic and thermodynamic properties of the materials are significantly altered from those of either the bulk or a single molecule. Among the above special properties of nanocrystals, the melting point of nanocrystals $T_m(r)$ with r being the radius of nanocrystals is one of the important thermodynamic characteristics, which determines many properties of materials. It is found that $T_m(r)$ is size-dependent and is evidently lower than the corresponding bulk one $T_m(\infty)$ [2–10]. Since noble metals have good corrosion resistance and thermal stability, the measured $T_m(r)$ functions have thus better measuring accuracy even the size of the crystals is only several nanometers. The above characteristics of the noble metals lead to that the measured $T_m(r)$ functions of these metals can be utilized to check up the validity of theoretical models and the computer simulation results for $T_m(r)$ functions. Thus, $T_m(r)$ functions of the noble metals are always measured for more than 30 years [6–9].

2. Model

Recently, a model without any free parameter for $T_m(r)$ was developed based on assumption on the size-dependent amplitude of the atomic thermal vibrations of nanocrystals in terms of Lindemann's criterion [11] and Mott's equation for the relationship between the vibrational part of the overall bulk melting entropy $S_{\text{vib}}(\infty)$ and $T_m(\infty)$ [12,13]. In this contribution, the experimental and computer simulation results of $T_m(r)$ functions of noble metals are compared with the prediction of this model. It is found that there is a good agreement among them.

$T_m(r)$ functions can be deduced by considering the averaged mean square displacement (msd) of a nanocrystal $\sigma^2(r)$ with [2]:

$$\sigma^2(r) = \sigma_V^2(r) + [\sigma_S^2(r) - \sigma_V^2(r)] \left(\frac{n_S}{n_V} \right) \quad (1)$$

where the subscripts S and V denote surface atoms and atoms located within the particle, n is the number of atoms in the nanocrystal with $n_S/n_V = (4\pi r^2 h/v)/[(4/3)\pi r^3/v - (4\pi r^2 h/v)] = 3h/(r - 3h)$ when the nanocrystal is considered as a spherical or quasi-spherical where v and h show the atomic volume and the atomic diameter. Since for nanocrystals the atomic oscillation of larger amplitude in comparison with the corresponding bulk value exists not only in the surface, but also in the core, it is assumed that: (1) $\sigma_V^2(r)$ and $\sigma_S^2(r)$ are size-dependent, $\sigma_S^2(r)/\sigma_V^2(r) = \sigma_S^2(\infty)/\sigma_V^2(\infty) = \alpha$ is however size-independent; (2) the cooperative coupling between the surface region and the interior region, which

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may be important for small particles and is considered phenomenologically by taking the variation of $\sigma^2(r)$ to be dependent on the value of $\sigma^2(r)$ itself [2]. With the above two considerations, a change in σ^2 can be given by [2]:

$$\sigma^2(x + dx) - \sigma^2(x) = (\alpha - 1)\sigma^2(x) dx \quad (2)$$

where $x = n_S/n_V = r_0/(r - r_0)$, $r_0 = 3h$ denotes a critical radius at which almost all atoms or molecules of a low-dimensional material are located on its surface. Integrating Eq. (2):

$$\int_{\infty}^r \frac{1}{\sigma^2(x)} d\sigma^2(x) = (\alpha - 1) \int_0^x dx$$

it is obtained:

$$\frac{\sigma^2(r)}{\sigma^2(\infty)} = \exp[(\alpha - 1)x] = \exp\{(\alpha - 1)/[(r/r_0) - 1]\} \quad (3)$$

r_0 has been further extended to all dimensions of the low-dimensional crystals [3–5]. Let d denote the dimension and $d = 0$ for nanoparticles where r has a usual meaning of radius, $d = 1$ for nanowires with r being taken as its radius and $d = 2$ for thin films with r denoting its half thickness [3–5]. r_0 is given by: (1) $r_0 = 3h$ for $d = 0$ since $4\pi r_0^2 h = 4\pi r_0^3/3$; (2) $r_0 = 2h$ for $d = 1$ since $2\pi r_0 h = \pi r_0^2$ and (3) $r_0 = h$ for $d = 2$ since $2h = 2r_0$. In short, the relationship between d and r_0 is given by [3–5]:

$$r_0 = (3 - d)h \quad (4)$$

To find a convenient means for correlating the size-dependent melting temperature $T_m(r)$ to measurable physical properties such as σ^2 , Lindemann criterion [6,7], which says that a crystal will melt when σ/h reaches a certain fraction of c , is useful and is known to be valid qualitatively for small articles:

$$\sigma/h = c \quad (5)$$

although c varies a bit with crystal structure: it is 0.13 for fcc crystal and 0.18 for bcc crystal [8]. This difference is partly induced by the change of h , which depends on the coordination number of the lattice CN [9]. A smaller CN corresponds to a smaller h [10]. In order to reduce or eliminate this difference among distinct lattices or CNs, h here is calculated by atom volume that is little dependent on the lattice structure [9]. With this h , c is almost a lattice-independent.

Since $T_m(r)$ is usually higher than the bulk Debye temperature $\Theta_D(\infty)$, the high temperature approximation can be utilized [2,11,12], $\sigma^2(r, T) = f(r)T$, where $f(r)$ is a size-dependent function. Thus, at any T , $\sigma^2(r, T)/\sigma^2(\infty, T) = f(r)/f(\infty)$. Moreover, when $T = T_m$, $f(r)/f(\infty) = \{\sigma^2[r, T_m(r)]/h^2\}/\{\sigma^2[\infty, T_m(\infty)]/h^2\}$ [$T_m(\infty)/T_m(r) = T_m(\infty)/T_m(r)$] in terms of Eq. (5) if the size dependence of h is neglected. In summary:

$$\frac{T_m(r)}{T_m(\infty)} = \exp\left[\frac{-(\alpha - 1)}{(r/r_0) - 1}\right] \quad (6)$$

In Eq. (6), α has been deduced for low-dimensional materials with free surface as follows [5]:

$$\alpha = \frac{2S_{\text{vib}}(\infty)}{3R} + 1 \quad (7)$$

where $S_{\text{vib}}(\infty)$ denotes the vibrational melting entropy and R shows the ideal gas constant. Since the overall bulk melting entropy $S_m(\infty)$ consists, at least, of three components: configurational entropy $S_{\text{conf}}(\infty)$, vibrational $S_{\text{vib}}(\infty)$ and electronic $S_{\text{el}}(\infty)$ [5], $S_m(\infty) = S_{\text{vib}}(\infty) + S_{\text{conf}}(\infty) + S_{\text{el}}(\infty)$. $S_{\text{conf}}(\infty)$ is given by [5], $S_{\text{conf}}(\infty) = -R(x_A \ln x_A + x_B \ln x_B)$ where x_A and x_B are the molar fractions of the crystals and vacancies, respectively, with an assumption that the melting of crystals leads to solely additional vacancies in liquid while the crystals remain a quasi-crystalline structure [13]. For the melting process, $x_A = 1/(1 + \Delta V_m/V_s)$, $x_B = 1 - x_A$ where $\Delta V_m = V_l - V_s$ with V_l and V_s being molar volume of liquid and crystal, respectively. For metallic, organic and polymer crystals, the type of chemical connection does not vary during the melting transition [13]. Thus, $S_{\text{el}}(\infty) \approx 0$ [5] and $S_{\text{vib}}(\infty) = S_m(\infty) - S_{\text{conf}}(\infty)$, or:

$$S_{\text{vib}}(\infty) = S_m(\infty) + R(x_A \ln x_A + x_B \ln x_B). \quad (8)$$

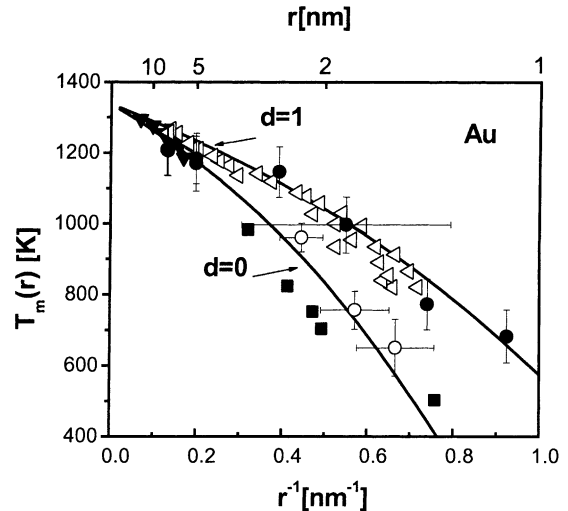


Fig. 1. $T_m(T)$ functions of the radius of Au crystals denoted as a solid line in terms of Eqs. (4), (6)–(8). (\triangleleft) [14], (\blacktriangledown) [15], (\bullet) [16] and (\circ) [17] denote experimental results while (\blacksquare) [18] shows a computer simulation result. The necessary parameters in Eqs. (4), (6)–(8) are as follows: $h = 0.2884 \text{ nm}$ [9], $T_m(\infty) = 1337.58 \text{ K}$ [19] and $S_{\text{vib}}(\infty) = 7.78 \text{ J mol}^{-1} \text{ K}^{-1}$ determined by Eq. (8) with $\Delta V_m/V_s = 5.1\%$ [20] and $S_m(\infty) = 9.38 \text{ J mol}^{-1} \text{ K}^{-1}$ [19]. $d = 0$ for the experimental result [17] and the computer simulation result [18] where the particles have a sphere shape. $d = 1$ for experimental data [14,15] where the particles are deposited on inert substrates in a disk-like shape, which have a quasi-dimension of one [3]. In another experiment [16], silica-encapsulated sphere particles are measured. Since the particles have not free surface, the corresponding α is smaller than $2S_{\text{vib}}(\infty)/(3R) + 1$ shown in Eq. (7). Because the decrease of α has the same effect of increase of r_0 as seen in Eq. (6), $d = 1$ is taken to avoid any detailed analysis with some assumptions on the chemical interaction between the surface atoms and the silica [16].

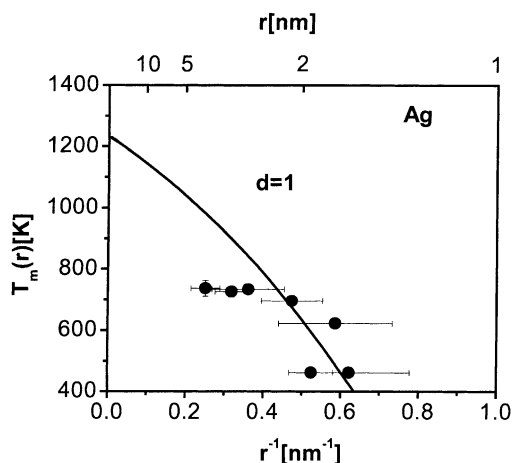


Fig. 2. $T_m(r)$ functions of the radius of Ag crystals denoted as a solid line in terms of Eqs. (4), (6)–(8). (●) shows the experimental results [16]. The related parameters in the above equations are: $h = 0.2989$ nm [9], $d = 0$, $T_m(\infty) = 1234$ K [19], $S_{\text{vib}}(\infty) = 7.98$ J mol $^{-1}$ K $^{-1}$ determined by Eq. (8) with $\Delta V_m/V_s = 3.3\%$ [20] and $S_m(\infty) = 9.16$ J mol $^{-1}$ K $^{-1}$ [19].

3. Results and discussion

In light of Eqs. (4), (6)–(8), $T_m(r)$ function is obtained. Figs. 1 and 2 present comparisons between the model predictions and the experimental and computer simulation results of $T_m(r)$ for Au and Ag nanoparticles. As shown in the figures, the model predictions are in good agreements with the both experimental and computer simulation evidences where $T_m(r)$ decreases as r and d decrease.

$T_m(r)$ is usually considered as a linear relationship between $T_m(r)$ and $1/r$ simply deduced by consideration on the surface/volume ratio, i.e. the ratio between the surface area and volume, which implies that the physical properties of atoms within the nanocrystals are the same of that of the corresponding bulk crystals and the melting point depression may be induced solely by the increase of surface atom percentage as the size of the nanocrystals decreases [5]. The effect of dimension on $T_m(r)$ comes from the same consideration since the surface/volume ratio is different for different dimensions. In our model, size-dependence of $T_m(r)$ is stronger than the above linearity when r is in the mesoscopic size range (when $r < 5$ nm). This non-linearity between $T_m(r)$ and $1/r$ in Eq. (6) is produced by our essen-

tial assumption that α is size-independent [2,5], which implies that the interior atoms of nanocrystals have additional contribution on the melting temperature depression.

4. Summary

In summary, our model for the size- and dimension-dependent melting temperatures of low-dimensional crystals is introduced to predict that of noble crystals. The predictions correspond to the experimental results and computer simulation results of Au and Ag nanocrystals well.

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