Modeling the Lattice Volume Effect on the Melting Temperature of Gold Nanoparticles

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الملخص

تم في هذا البحث تعديل النمـــوذج المستند على التذبذب الشبيكي لاجل استخدامه في تخمين مدى اعتماد درجة الانصهار على الحجم ومعدل مربع الازاحة لجسيمات الذهب النانوية الحرة, اثبت النموذج على ان نقطـة الانصهار تقل بنقصان حجم الجسيمات النانوية نتيجة التغيير في حجم الـشبيكة للجسيمات. كانت النتـائج المحسوبة مطابقـة للنتـائج العمليـة المتوفرة لجسيمات الذهب النانوية.

Abstract

The modification of lattice vibration based model used to predicate the dependence of melting temperature on the size and mean square displacement of the free standing gold spherical nanoparticle. The models predicate that the melting temperature decreases with the reduce of nanoparticles size due to the change of its lattice volume, calculated values of melting agree fairly well with the available experimental data of Au nanoparticles.

1- Introduction

One of the main interests of the current research is the understanding and the engineering of the condensed matter at low dimensions. Low dimensional materials lie between bulk matter, molecular and atomic sizes. In a size scale of nanometers, materials in this regime exhibit novel physical and chemical properties and these because atoms have a chemical environment completely different from the ones in the interior of the structure [1, 2].

The metallic nanoparticle melts below their corresponding bulk melting temperature. This happens because surface atoms prefer to reach earlier the liquid state, where can minimize their energy. The decrease in

melting temperature is approximately dependent on the inverse of the nanoparticles radius and theses due to the surface effect and the energetic changes of atoms within crystals [3].

In this work, an attempt will be made to modulate a method for calculating nanoparticles lattice volume and then evaluate its effects on the melting applicable on gold nanoparticles.

2- Method of calculation

This model (lattice vibration based model) of the melting point of nanoparticles is based on the Lindemann criterion which states that a crystal will melt when the root – mean square displacement of the atoms in the crystal (α) exceeds a certain fraction of the inter-atomic distance d [4]. Lindeman proposed a melting model using the theory of simple harmonic vibration of an atom. The average atomic thermal vibration energy in Lindeman's model can be expressed as [4]:-

$$M(2\pi v_E)^2 \sigma^2 = k_B T \tag{1}$$

Where M is the mass of the atom, v_E is the Einstein frequency, σ^2 is the root-mean-square thermal average amplitude, k_B is the Boltzmann constant, and T is the absolute temperature.

According to Lindeman assumption, crystal will melt when the root – mean square displacement of the atoms in the crystal (α) exceeds a certain fraction of the inter-atomic distance d_{mean} [5], then the following equation can be obtained, which relates to the bulk melting point T_∞, that is, [6,11]:

$$\theta_D = c\left[\frac{T_\infty}{MV^{2/3}}\right]^{1/2} \tag{2}$$

In this equation, θ_D is the size dependent Debye temperature, c is a constant value, M is the mass of the atom, and V is the lattice volume. In terms of the Deby model, the θ_D function is related to the root-mean-square σ by [7],

$$\sigma^2(r,\ T)\ \alpha\ T/\theta_D^2(r)$$

The melting point depression of the nanoparticles is roughly proportional to their reciprocal of radius r written as [5, 11].

$$T_r/T_\infty = 1 - C/r \tag{3}$$

Where C denotes an unknown material constant. T_r / T_∞ functions can be deduced by considering the average mean square displacement (*msd*) of atoms in a nanoparticle with $\sigma^2(r)$ [6-11], T_r is the particle melting temperature and T_∞ is that of the bulk.

The relationship of the mean square displacement of the nanoparticles size can be expressed as;

$$n\sigma^2(r) = n_v\sigma_v^2(r) + n_s\sigma_s^2(r)$$

or $\qquad \sigma^2(r) = \left(\frac{n_v}{n}\right)\sigma_v^2(r) + \left(\frac{n_s}{n}\right)\sigma_s^2(r) \tag{4}$

In this equation, s and v denotes the surface and interior atoms of a nanoparticles, $\sigma^2(r)$ is the average value of the vibration mean square amplitude. n_s denote the number of atoms at the surface, n_v is the number of interfacial atom, n is the atom number of a nanoparticles with:

$n_s/n_v = (4\pi r^2 h) / [(4/3)\pi r^3 - (4\pi r^2 h)] = 3h/(r-3h)$

when the shape of the particle considered to be spherical or quasi-spherical and h is the surface atomic diameter of a nanoparticles[11].

Equation.4, shows that the total mean square displacement of atomic vibration can be divided into two parts, surface and interior. Because the interfacial atoms have (surface atoms for nanoparticles) a higher free energy, melting often starts at the interface.

With particle size r increasing, on condition that the volume of the lattice is fixed, the relative ratio of surface to interior (n_s/n_v) is increased. The higher free energy of the interior atom will produce, the increase of its melting temperature and accordingly the dependence of $\sigma^2(r)$ on r all give the following [6]:-

1) The ratio between $\sigma_s^2(r)$ and $\sigma_v^2(r)$ has a constant value, and denoted as:

$$\frac{\sigma_s^2(r)}{\sigma_v^2(r)} = \frac{\sigma_s^2(\infty)}{\sigma_v^2(\infty)} = \alpha$$

Here $r = \infty$ corresponding to the bulk material.

2) A new parameter r_c is defined, which corresponds to the case that all atoms are located at the surface according to the Friedels nucleation theory [6, 11], when particle size is less than a critical dimension of the crystal nucleus, the melting temperature will be zero. So a crystal can exist only when the diameter is greater than this size. Based on this assumed parameter, the ration between n_s and n_v will be [11]:-

$$x = \frac{n_s}{n_v} = \frac{r_c}{(r-r_c)}$$

Based on the above two conditions, the cooperative coupling between the surface region and the interior region may be important for small particles, the variation of $\sigma^2(r)$ is considered phenomenologically to be dependent on the value of $\sigma^2(r)$ it self [11], which leads to;

$$\sigma^2(x+dx) - \sigma^2(x) = (\alpha - 1)\sigma^2(x)\,dx \qquad (5)$$

Where $x = n_s/n_v = r_c/(r-r_c)$, with $r_c = 3h$ the critical radius of order $3h$ represents a length scale characteristics for the crystllinity[20]. Integrating Eq. 5, from the definition of natural logarithm;

$$\ln x = \int_1^x \frac{1}{\sigma^2(x)}\, d\sigma^2(x), \, x > 0$$

Then;

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

$$\ln \; \sigma^2(r) - \ln \; \sigma^2(\infty) = (\alpha - 1)(x - 0)$$

$$\ln\left(\frac{\sigma^2(r)}{\sigma^2(\infty)}\right) = (\alpha - 1)x$$

$$x = \frac{r_c}{(r - r_c)} = \frac{1}{\left(\dfrac{r}{r_c} - 1\right)}$$

$$\sigma^2(r) / \sigma^2(\infty) = exp\,[(\alpha - 1)x] = exp[(\alpha-1)/(r/r_c-1)] \tag{6}$$

Where r_c is a critical radius of a nanoparticle, in this case all atoms are located on the surface [11], From Eq. 2, where $T_\infty \; \alpha \; \theta_D^2(\infty) \; V_\infty^{2/3}$,Eq. 2, can be extended to nanometer size $Tr \; \alpha \; \theta_D^2(r) \; V_r^{2/3}$ and this combination will leads to [18, 19];

$$\frac{T_r}{\theta_D^2(r)V_{(r)}^{\frac{2}{3}}} = \frac{T_\infty}{\theta_D^2(\infty)V_{(\infty)}^{\frac{2}{3}}} \tag{7}$$

According to the Lindeman's criterion for melting and Motts equation [4, 6, 14], the size- dependent *rms* $\sigma(r)$ has been found to have the following form:

$$\frac{\sigma^2(r)}{\sigma^2(\infty)V^{\frac{2}{3}}(r)} = \exp\left[(1-\alpha)/(\frac{r}{r_c}-1)]\right] \tag{8}$$

$\sigma^2(r)\theta_D^2(r) = \sigma^2(\infty)\theta_D^2(\infty) =$ const, So Eq. 8, can also be written as [20];

$$\frac{T_r}{T_\infty} = \left(\frac{V_r}{V_\infty}\right)^{2/3} \exp\left[-(\alpha-1)/\left[\frac{r}{r_c}-1\right]\right] \tag{9}$$

According to reference [8], α is a thermal vibrational entropy and is equal to;

$$\alpha = [2 \; S_{vib}(\infty)/(3R)]+1$$

Then the relationship between nano size melting temperature and that of the bulk material can be shown by the following equation: [13, 16, 18].

$$\frac{T_r}{T_\infty} = \left[\frac{V_r}{V_\infty}\right]^{2/3} \exp\left[\frac{2\,S_{vib\,(\infty)}}{3\,R\,(\frac{r}{r_c}-1)}\right] \tag{10}$$

Melting entropy of bulk crystals S_m consists at least three components:- positional S_{pos}, vibrational $S_{vib,}$ and electronic S_{elc}. Namely, $S_m = S_{pos} + S_{vib} + S_{elc}$ [1,12]. S_{pos} arises due in connection with positional disorder as a substance undergoes a melting transition. For metallic crystals, the type

of chemical connection does not vary during the melting transition, thus $S_{elc} = 0$, and $S_{vib} = S_m - S_{pos}$

For low dimensional crystals r_c depended on dimension (d):- $d = 0$ 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 r_c is given by:-
(1) $r_c = 3h$ for $d = 0$ since $4\pi r^2_c h = 4\pi r^3_c /3$; (2) $r_c = 2h$ for $d = 1$ since $2\pi r_c h = \pi r^2_c$ and (3) $r_c = h$ for $d = 2$ since $2h = 2r_c$. The relationship between r_0 and atomic diameter h is shown as [13,17]:

$$r_c = (3-d)h \tag{11}$$

To evaluate how lattice volume in Eq.10, affects the melting temperature, it should first be calculated; in this case a relation which is reported by Omar and Taha [10] for Si nanowires as shown in figure 1, for Au nanoparticles is modified and used to evaluate such dependence.
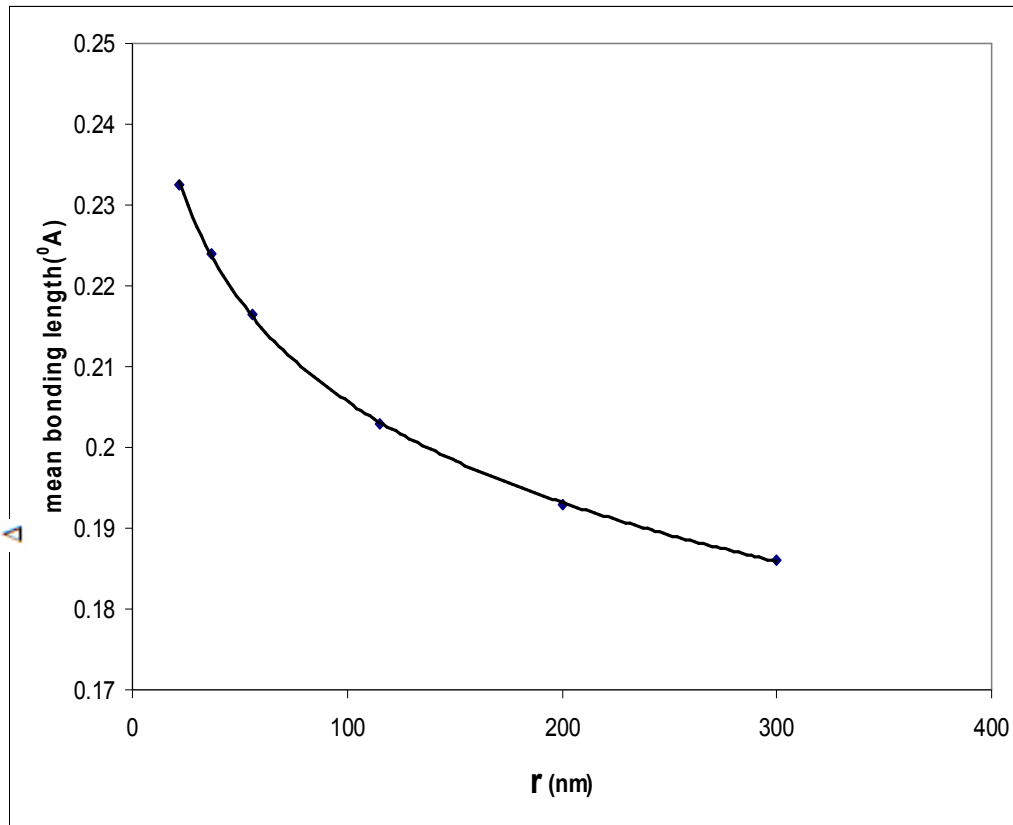

Figure 1: The mean bonding length (Δ d_{mean}) versus radius for silicon nanowires, where the data taken from ref [10]. For silicon, h=0.3338nm.

Figure 2, shows the melting point of gold nanoparticles as a function of their size by using different models, such as, lattice vibration based (LVB) model with and without the effect lattice volume due to Eq.10, also figure shows the homogenous melting (HM) model as well as of its modification [12,13,15].

There are good agreements between the experimental data and that obtained through Eq. 10, as shown in figure 2, however, for the diameter less than 5nm a phase change has been reported for nanoscale crystals and that consequently differs the lattice volume and entropy. In this case values of volume and entropy are no more suitable for such calculation for the melting.
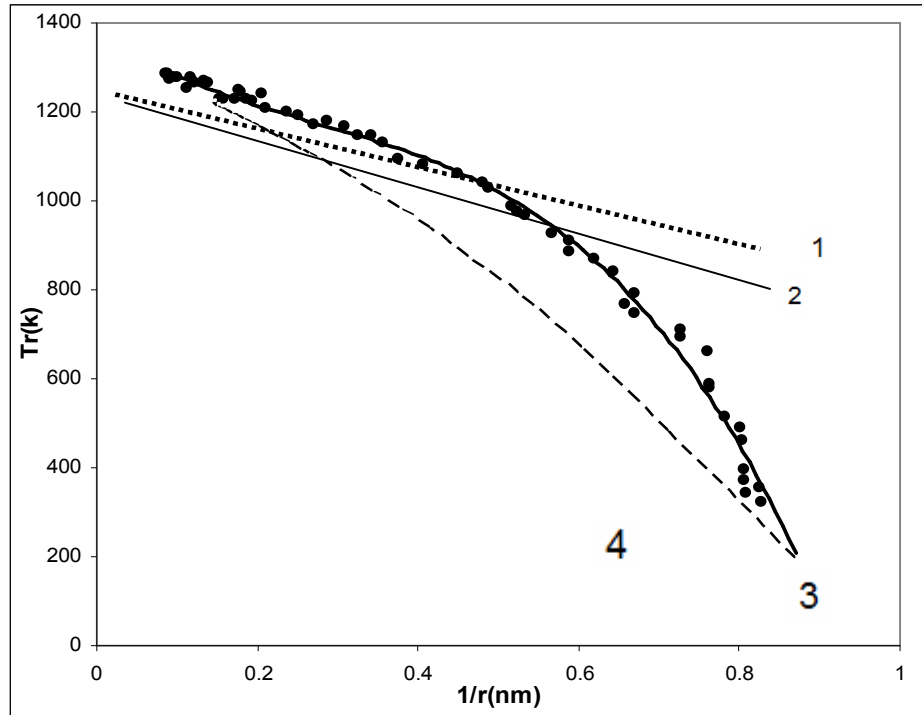

Figure 2: Melting point versus reciprocal radius for Au nanoparticles.

The symbols (•) represent the experimental data of gold nanoparticles taken from ref [15], and number (1) on the figure represent the homogenous melting (HM) model ref [12,13], (2) represent the modification homogenous model ref[12,13], (3) represent the lattice vibration based (LVB)model with effect of lattice volume Eq. (10), (4) LVB model without the effect of lattice volume ref[18], for gold; $T_{\infty}=$ 1337.58k, S_{vib}=7.78 J mol^{-1}k^{-1}, R= 8.314 Jmol^{-1}k^{-1}, and h=0.2884 nm

It is well known that the surface layered atoms have their inter-space distance of h which is for Au equal to 0.2884nm and its internal mean bonding length d_{mean} is 0.2224nm. According to this knowledge, the maximum change between the two cases is their difference. For simplicity the change in inter atomic distance is zero for bulk Au $\Delta d_{mean}(\infty) = 0$, for the critical volume of Au nanoparticles with, $d_{mean}(r_c)$ - $d_{mean}(\infty)=\Delta\ d_{mean}(r_c) = 0.0664$nm is mentioned earlier, where their relation is a power dependence. Through the method of trial and error the best relation for $\Delta d_{mean}(r)$ eq.12, dependence to give the best melting temperature dependence on size in figure 2, is found to be;

$$\Delta d_{mean}\ (r) = 0.066D^{-1.3756} \tag{12}$$

Figure 3, shows such dependence. Mean bonding length $d_{mean}(r)$ dependence on the size of nanoparticle and it can be calculated by the following equation;

$$d_{mean}(r) = d_{mean}(\infty) + \Delta d_{mean}(r) \tag{13}$$

Where $d_{mean}(\infty)$ mean bonding length of bulk, $d_{mean}(r) = h$, the inter planer distance between the two cases should have values between the two and d will be referred by $d_{mean}(r)$, then the change from $d_{mean}(\infty)$ to $d_{mean}(r)$ can be referred by $\Delta d_{mean}(r)$.

The mean bonding length d_{mean} dependence on the lattice constant can be determined according to the following relation [21];

$$d_{mean} = \frac{\sqrt{3}}{4}a \tag{14}$$

Where a is a lattice constant, a^3 is the unit cell volume (for 8 lattice volume). For gold, the bulk lattice volume V equal to 16.94 A as calculated from its density [22]. Figure 2, contains also the calculated curves due homogenous melting model and it is modification and comparison with experimental data [15].
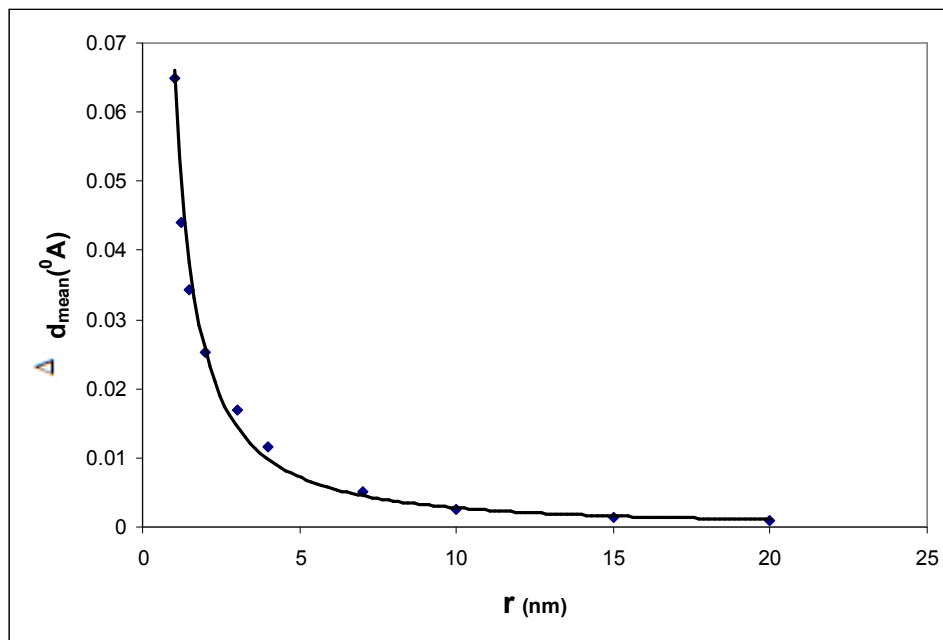

Figure 3: The change in mean bonding length versus radius for Au nanoparticles.

3- Conclusion

The formula for the nanoscale size dependent lattice volume for Si is modified successfully to work on Au nanoparticles. The modified model for melting temperature of nanoparticles due to the effect of lattice volume improves well the calculated curve to that of the melting experimental data melting taken from references.

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