EFFECTS OF SIZE AND SHAPE ON THERMODYNAMIC PROPERTIES OF NANOMATERIALS

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ABSTRACT

A simple model based on the cohesive energy of the Nano-material has been used to study the size dependence of Debye temperature and Young's modulus of Au, Ag, Ni and Pb nanomaterials.It is noted that the Debye temperature and the Young modulus both decreases with particle size of different shapes of nanomaterials. The results obtained were compared with available experimental data to determine the accuracy of the model. A good agreement between the theoretical model and experimental data is observed for the Debye temperature and Young's modulus for the considered nanomaterials.

Keywords: Nanomaterials, Young Modulus, Debye Temperature

I. INTRODUCTION

The idea of nanotechnology first appeared in the famous talk "there is plenty of room at the bottom." Given by the physicist Richard Feynman at the American Physical Society meeting at Caltech on December 29, 1959. Feynman anticipated and described a process by which scientists would acquire the ability to manipulate materials at a nanoscale, and indeed he was right because here we are the 21st century doing just that. The term nanotechnology was originally defined by Norio Taniguchi in 1974 as follows: "nanotechnology mainly consists of the processing of separation, consolidation and deformation of materials by one atom or by one molecule." Nanotechnology and nanoscience began in the early 1980's with the advances in computing power and material modeling. Nanomaterials are basically the link between nanoscience and nanotechnology. Nanomaterials generally deal with sizes less than 100nm [1].

According to Roduner, E. (2006), a small sample of gold has quite different properties from the ordinary gold we know. At 10nm, it is no longer shiny and yellow but instead it absorbs green light and appears red. It's melting temperature decreases drastically as size is decreased and it ceases to be noble. So, it is safe to say that elements we know are totally different at nanoscale, hence the birth of words such as nanomaterials, nanotechnology and nanoscience.This project is centered on the Debye temperature, but we will also include other nanomaterial properties briefly in this introduction. The Debye temperature $\theta_D(r)$ has received considerable attention because it is an essential property to characterize many materials properties such as thermal vibration of atoms and phase transitions. Furthermore, other important physical properties and their size-dependence such as the Einstein temperature $\theta_E(r)$ and volume thermal expansion coefficient $\alpha_v(r)$ are related to the Debye temperature. Thus once the Debye temperature is known, the others can be determined

from it. [3]There is a spectrum of frequencies that atoms in a crystal can assume, and the maximum frequency that the atoms can assume is called the Debye frequency. The Debye frequency can be attributed to a certain maximum temperature that can be achieved due to a single normal vibration and that is the Debye temperature given by:

$$\theta_D = \frac{h\nu_m}{K_B} \qquad (1)$$

Where h is the Plank's constant. K is the Boltzmann constant, ν_m is the Debye frequency

The results so far suggest show that the Debye temperature increases with increasing radius. [4]. A lot of experimental and theoretical studies have been conducted concerning effect of size on thermodynamic properties of nanomaterials. A theoretical study of size dependence of cohesive energy for Ag, Co, Al and Cu nanoparticles was conducted by Zhu et al. Cottie carried out the study of melting temperature and its dependence on size for Au Nano-crystalline. Olson et al on the other hand studied the size dependence of melting temperature of Bi Nano-film. Liang et al studied the size dependence of elastic modulus of Cu and Au thin films [5].Numerous studies have focused on the measurement of melting temperature $T_m(r)$ since Takagi first observed the size-dependence of melting temperature for metallic nanoparticles. The methods used to measure $T_m$include: electron diffraction, particle shape change, and dark field image, scanning Nano-calorimetry, in situ X-ray diffraction and many more. The results showed that T_m decreases with decreasing r for isolated Nano-solids with free surfaces, which is called "undercooling" as opposed to thermodynamic "superheating". Couchman & Jesser suggest that melting of small particles is a liquid nucleation and growth process. With melting beginning by nucleation of liquid at the surface and the liquid nucleus moves into the solid with an activation energy. [4]. A size-dependent elastic properties study for ZnO nanowires by Hu, J. Liu, W. & Pan, B.C.showed that total energy of nanowires increase as the radius decreases and that the total energy is higher than that of bulk ZnO. Implying that smaller nanowires are less stable. The study also showed that Young's modulus increases monotonically as the radius decreases. Furthermore, when the size of a ZnO nanowire becomes large enough, its Young's modulus should approach the bulk value. However the fact that values of Young's modulus are higher than the bulk value suggests that the ZnO nanowires are stiffer than the bulk ZnO. However this can only be seen at the surface, meaning as we go inside the nanowire wire it becomes softer than the surface. Hu concluded that this was caused by the compressive strain of the surfaces and that the softening of the interior layers has stemmed from their tensile strain.

With the development of nanoscience and nanotechnology in recent years, size of materials come into nanometer size range (<100nm) at least in one dimension. This leads to dramatic increase of surface/volume ratio and corresponding changes of physical, chemical and mechanical properties. It is very important to understand these properties and their related physical basis for correct industrial application.

With that being said, the purpose of the project is to determine the Debye temperature and Young's modulus of the nanomaterials which is based upon the cohesive energy of the nonmaterial. For that I studied the equation of states for the size dependent Debye temperature of the following nanomaterials: Au, Ag, Ni and Pb. This will be carried out for spherical nanosolid, nanowire and nanofilm. The results will then be compared to experimental data in order to determine the accuracy of the model used. The idea behind this research is to provide better understanding of properties of nanomaterials for optimum application and to make an addition on the existing literature regarding the subject of nanomaterials and their properties.

II. THEORETICALMODEL

The cohesive energy of the nanomaterials is the sum of energy due to the contributions of the interior atoms and the surface atoms, which is expressed as

$$E_{sum} = E_0(n - N) + \frac{1}{2}E_0 N \qquad (2)$$

Where n is the total number of atoms of Nano-solids and the number of its surface atoms is N .

Therefore, $(n - N)$ is the total number of interiors atoms of the Nano-materials. E_0 Is the cohesive energy of the bulk materials per atom. Eq. (1) may be written as

$$E_p = E_b(1 - \frac{N}{2n}), \qquad (3)$$

Where E_p is the cohesive energy per mole of the nanomaterials, which is given by $\frac{AE_{sum}}{n}$, here, A is the Avogadro constant. E_b is defined as the cohesive energy per mole of the corresponding bulk materials which is given by $E_b = AE_0$.

The relation between the melting point of nanomaterials and bulk are reported as:

$$T_p = T_b\left(1 - \frac{N}{2n}\right) \qquad (4)$$

The elastic moduli increase by increasing the cohesive energy. The relation for elastic moduli can be written as

$$B_p = B_b\left(1 - \frac{N}{2n}\right) \qquad (5)$$

And

$$Y_p = Y_b\left(1 - \frac{N}{2n}\right) \qquad (6)$$

One may get the connection between the melting point and the Debye temperature from the Lindemann's comparative. According to this a crystal will melt when the root mean square displacement of an atom exceeds a certain fraction of the interatomic distance in the crystal. Relating the specific heat theory with the Lindemann's melting formula, the characteristic temperature square is proportional to the melting point of the crystal. So, the Debye temperature for the bulk material is inscribed as

$$\theta_b^{\,2} \propto \left(\frac{T_b}{MV^{2/3}}\right), \qquad (7)$$

Similarly, for nanomaterial

$$\theta_p^{\,2} \propto \left(\frac{T_p}{MV^{2/3}}\right), \qquad (8)$$

Where, M is the molecular mass.

Equation (7) and (8) give the following relation we get

$$\left(\frac{\theta_p^2}{\theta_b^2}\right) = \frac{T_p}{T_b} \qquad (9)$$

One can derive the relation for α_p, which is recited as

$$\alpha_p = \alpha_b \left(1 - \frac{N}{2n}\right)^{-1} \qquad (10)$$

Therefore, from Eq. (5) and (6) we acquire

$$\left(\frac{\theta_p}{\theta_b}\right) = \left(1 - \frac{N}{2n}\right)^{1/2} \qquad (11)$$

Where, N is the total number of surface atoms and n is the total number of Nano-solids. α_b is coefficient of volume thermal expansion of bulk material. The surface atoms refer to the first layer of the Nano-solid. The method to find $N/2n$ for different shape of nanomaterials has been calculated. The value of $\frac{N}{n}$ is $\frac{4d}{D}, \frac{8d}{3l}$ and $\frac{4d}{3h}$ for spherical Nano-solids, nanowires and Nano-films respectively. Where, d is the diameter of Nano-solid and D is the diameter of the spherical Nano-solids. l and h are the diameter of nanowire and height of the Nano-film correspondingly.

Table 1. Input Parameters

Nano-material	Atomic diameter (d nm)
Au	0.3189
Pb	0.3869
Ni	0.2751
Ag	0.319

III. RESULTS AND DISCUSSION

From the figures we can see that Young's modulus, specifically the ratio increases. The graph can be divided into two parts, which are sizes less than 10nm (D, L, H < 10) and sizes greater than 10nm (D, L, H >10) [6]. There is a drastic change in Young's modulus for sizes less than 10nm but there is a gentle change, which tends to be constant for bigger sizes. The drastic change can be attributed to surface area and volume ration, which is given by:

$$\frac{A}{V} = \frac{3}{r} \qquad (16)$$

Where r is the radius of the sphere for spherical Nano-solid. The r can be replaced by L or H for nanowire and Nano-film respectively. Most of the physical properties of nanomaterialsare a result of high surface area to volume ratio. From equation (5) it can be seen that the ratio decreases as r increases, and if r is very large the ratio become very small. Thus when D, L, H <10nm, the area to volume ratio is larger hence the drastic increase

in Young's modulus. For D, L, H >10nm, the area to volume ratio is decreasing hence the gentle increases of Young's modulus, which becomes a constant for very large r values.

This is because at very large r values, the influence of the area to volume is negligible if not zero and the materials have now shifted from being nanomaterials to ordinary bulk materials.

A study conducted by Patil, S.D et ol (2014), which involved effect of size and shape on Young's modulus by Lindeman's criterion show rather opposite results to ours. He did use a different model given by:

$$\frac{Y_n(r)}{Y_b(\infty)} = \exp\left[\pm \frac{(\alpha - 1)}{(r/r_0 - 1)}\right] \quad (17)$$

Which lead me to believe that Young's modulus does not show a universal trend with particle size as the literature shows. That perhaps the variation trend depends strongly on the application conditions.

Another study by Dabhi, S. & Jha, P.K. which is very similar to ours used the same model for Young's modulus, given by:

$$Y_n = Y_b\left(1 \pm \frac{N}{2n}\right) \quad (18)$$

Where they explained that the positive and negative signs are the representation of orientations. Meaning the plus or minus sign can go either way, because for our study we used the minus sign. According to Dabhi, S. & Jha, P.K. recent studies on mechanical properties with size for TiO_2, SnO_2 and CeO_2 do not reach to a universal conclusion regarding the size dependency of Young's modulus in these compound despite their possible uses in Nano-electric systems and resistance based gas sensors as active components. This shows that the mechanism for size dependency of Young's modulus in 1D nanomaterials is not well understood and a systematic effort is desired [8].From the figures, Debye temperature follows the same general trend as the Young's modulus. Meaning Debye temperature increases as particles size increases. The graph still exhibits two parts, D, L, H<10nm and D, L, H >10nm. Similarly these parts can be attributed to surface area to volume ratio like with Young's modulus. The only difference is that the graph for Debye temperature is much steeper than that of Young's modulus. Perhaps this is because the Debye temperature is much more sensitive to change in surface area to volume ratio.

Unlike the Young's modulus, all the studies I reviewed showed similar results for Debye temperature, thus the Debye temperature is bit a sure thing than the Young's modulus. The experimental results for Au thin films are included and as it can be seen there is a very good agreement between our models results and the experimental results.

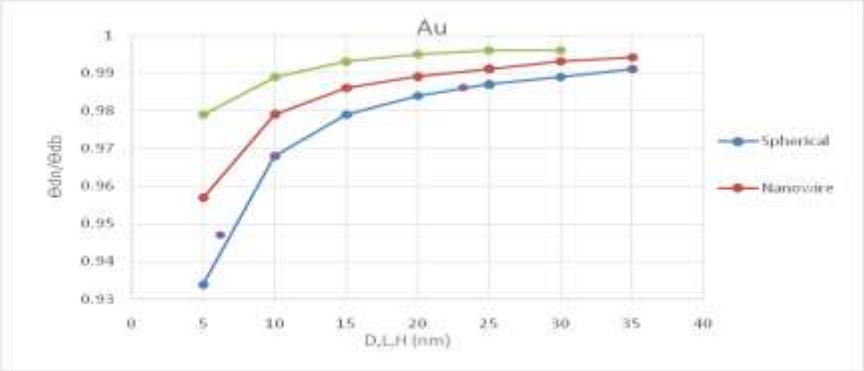

Fig.3 Size Dependence of the Ratio of Debye Temperature for Au Nano-Particle

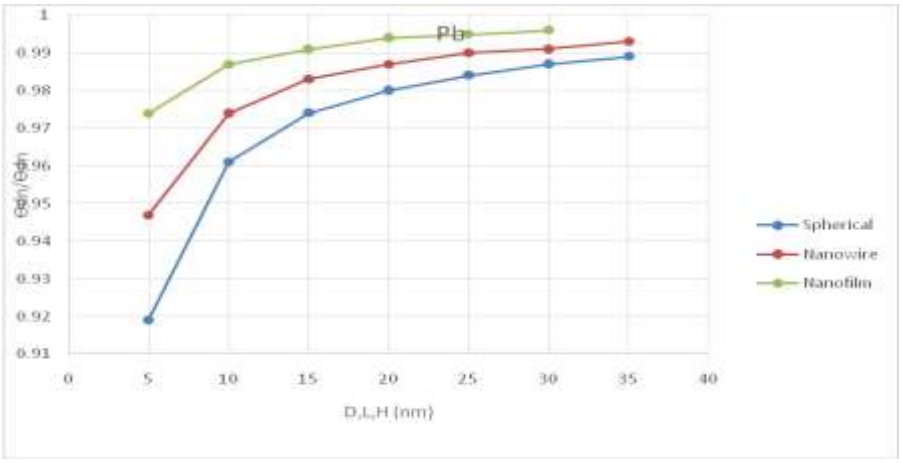

Fig.4. Size Dependence of Debye Temperature Ratio for Pb Nano-Particle

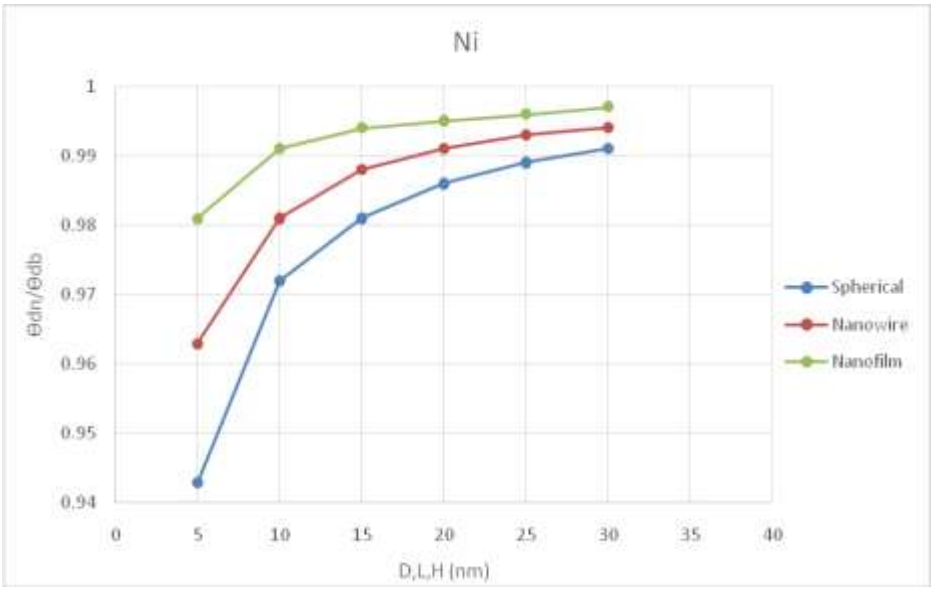

Fig.5. Size Dependence of Debye Temperature Ratio for Ni Nano-Particle

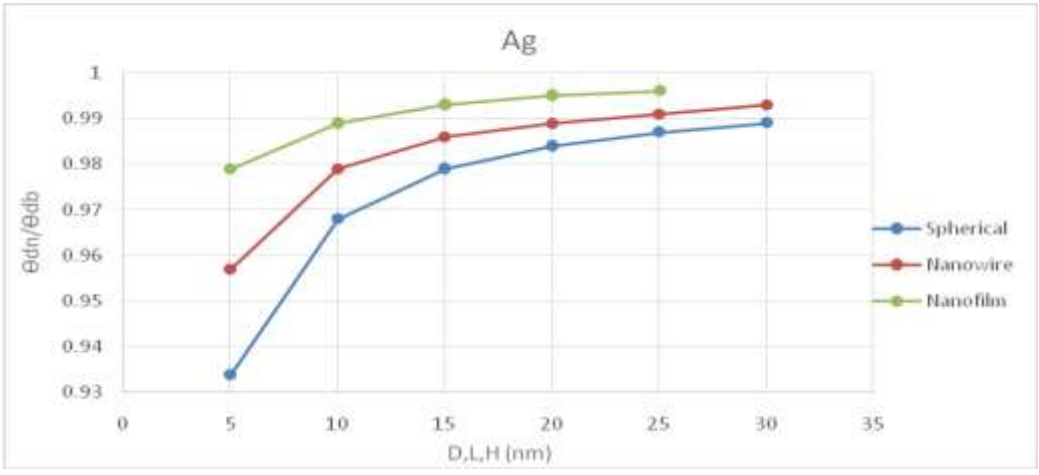

Fig.6. Size Dependence of Debye Temperature Ratio for Ag Nano-Particle

Young's modulus

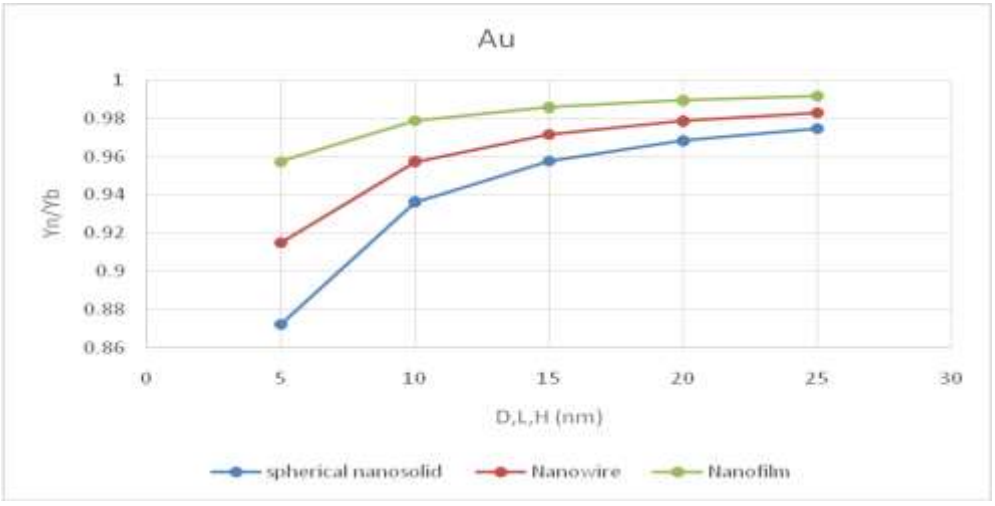

Fig.7. Size Dependence of the Young's Modulus Ratio for Au Nano-Material

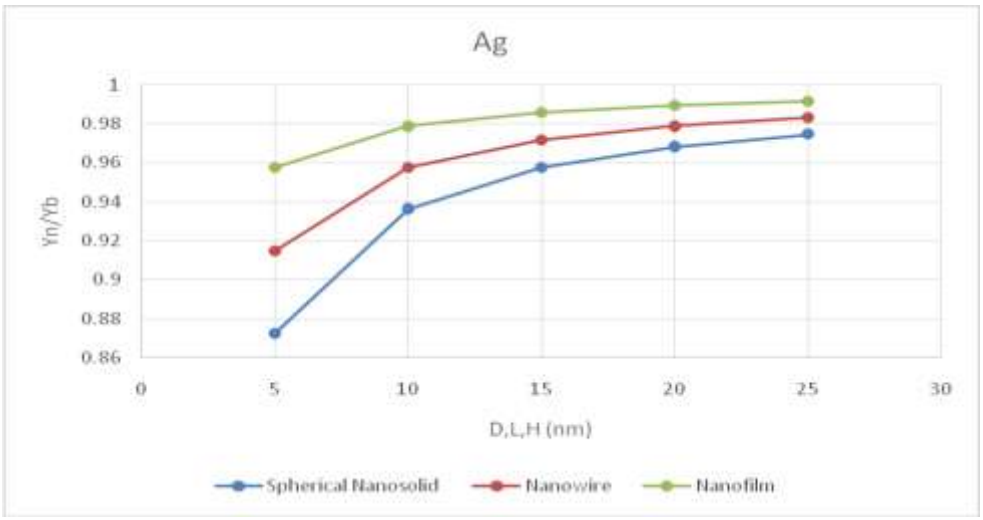

Fig.8. Size Dependence of Young's Modulus Ratio for Ag Nano-Material

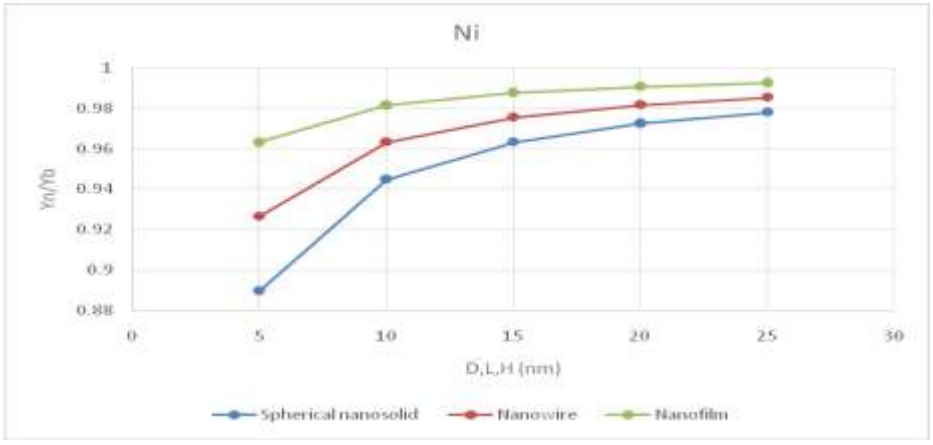

Fig.9. Size Dependence of Young's Modulus Ratio for Ni Nano-Material

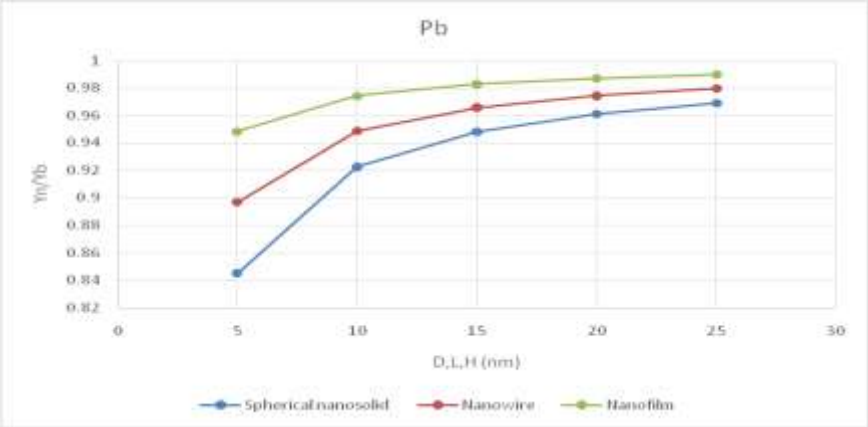

Fig.10. Size Dependence of Young's Modulus Ratio for Pb Nano-Material

IV. CONCLUSION

In conclusion, both the ratio of Young's modulus and Debye temperature ratio increases with increasing particle size. However, both the graphs of Young's modulus and Debye temperature can be divided into two parts (D, L, H<10nm & D, L, H>10nm). For D, L, H<10nm the two properties show rapid increase with increasing size and for D, L, H>10nm the increase is gentle until it becomes a constant at very large atomic sizes.

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