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Effect of size on the elastic and thermodynamic properties of nanomaterials

Jeewan C Bhatt[1] & Kuldeep Kholiya[2]

[1]Department of Applied Science, G B P Engineering College, Ghurdauri, Pauri Garhwal, Uttarakhand, India

[2]Department of Applied Science, B T Kumaon Instituite of Technology, Dwarahat, India

E-mail:jeewan25may@rediffmail.com

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Simple theoretical model has been proposed to study the size dependence of thermodyamic properties i.e. melting temperature, Debye temperature and elastic properties i.e. bulk modulus, Young modulus, thermal expansion coefficient. The model is then applied to Pb spherical nanosolid, Au nanowire and Fe spherical nanosoid. On comparing with available experimental findings, the results obtained in the present study give a close agreement and hence, demonstrate the validity of the method proposed in the present paper.

Keywords: Elastic properties, Nanomaterials, Thermodynamic properties

1 Introduction

As the field of nanoscience and nanotechnology has developed in recent years, size of materials has reduced into nanometer size range at least in one dimension, which lead to dramatic increase of surface (interface) to volume ratio and corresponding changes of physical, chemical and mechnical properties. The most important characteristic of a nanomaterials is its size effect, i.e., the properties of a nanoparticle are different from the corresponding bulk material[1-4]. The cohesive energy also known as the heat of sublimation is an important physical quantity to account for the strength of metallic bonds, as it is the energy to divide the metallic crystal into individual atoms. Experimental study of size dependence of cohesive energy of *W* was carried out by Kim *et al*[5]. and Xiao *et al*[6]. Hou *et al*[7]. studied the size dependence of cohesive energy of Ag and Co nanoparticles using computer simulations. A theoretical study of size dependence of cohesive energy for Ag, Co, Al and Cu nanoparticles was carried out by Zhu *et al*[8]. Qi *et al*[9]. studied the size effect on the cohesive energy of Cu nanoparticle.

The size dependence of melting temperature of nanocrystalline Au has been studied by Cottie[10]. Wang *et al*[11]. have studied the size dependence of melting behaviour of Zn nanowire using X-ray diffraction and transmission electron microscopy. Olson *et al*[12]. studied the size dependence of melting temperature of Bi nanofilm. Sun *et al*[13]. studied the size dependence of melting temperature of Al nanoparticle.

Liang *et al*[14]. studied the size dependent elastic modulus of Cu and Au thin films and suggested that elastic modulus of metallic free thin films increases as the thickness of the film decreases. Lihong *et al*[15]. studied the size dependent elastic modulus and vibration frequency of nanocrystals and concluded that the elastic modulus and the vibration frequencty of metal,ceramic and semiconductor nanocrystals are dependent on the thickness of thin film and the diameter of nanoparticle. Hu *et al*[16]. studied the size dependent elastic properties of ZnO nanowires and nanotubes. Zhao *et al*[17]. studied the size effect on thermal properties in low dimensional materials.

A hypothetical model about the size dependence of cohesive energy and melting temperature has been reported by Qi[18]. The model has been found quite satisfactory. In the present work, the model is extended to study the size dependence of thermorelastic properties of nanomaterials viz. thermal expansion coefficient, Young modulus, bulk modulus, melting temperature and Debye temperature.

2 Method of Analysis

The total cohesive energy of the nano crystalline solid due to the contributions of the surface atoms as well as the interior atoms may be written as follows[18]:

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

where E_0 is the cohesive energy per atom of the corresponding bulk material, n the total number of atoms in a nano crystalline solid and N is the number

of surface atoms. To determine cohesive energy per mole Eq. (1) may be rewritten as:

$$\frac{AE_{tot}}{n} = AE_0\left(1-\frac{N}{n}\right)+\frac{AE_0N}{2n} \quad \ldots(2)$$

where A is the Avogadro number.

Thus, $\frac{AE_{tot}}{n}$ represents the cohesive energy per mole of the nano crystalline solid (E_n) and AE_0 is the cohesive energy per mole of the corresponding bulk material (E_b). Substituting these values in Eq. (2) gives:

$$E_n = E_b\left(1-\frac{N}{2n}\right) \quad \ldots(3)$$

As the cohesive energy has the linear relation to the melting temperature[19,20], the melting temperature of the nano crystalline solids can be written as:

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

where T_{mn} and T_{mb} are the melting temperatures of nano crystalline solid and corresponding bulk material, respectively.

Using the Lindemann[19] criterion of melting which states that a crystal melts when the root mean square displacement of atoms in the crystal exceeds a certain fraction of the interatomic distance the relationship between the melting temperature (T_m) and the Debye temperature (θ_D) of the crystal[20] can be written as follows :

$$\theta_D = \text{const}\left(\frac{T_m}{MV^{2/3}}\right)^{1/2} \quad \ldots(5)$$

where M is the molecular mass and V is the volume per atom. Using Eq. (12), Liang and Baowen[21] reported the following relation:

$$\left(\frac{\theta_{Dn}}{\theta_{Db}}\right)=\left(\frac{T_{mn}}{T_{mb}}\right)^{1/2} \quad \ldots(6)$$

where θ_{Dn} is Debye temperature of nanomaterials and θ_{Db} is the Debye temperature of corresponding bulk material. In view of Eq. (4), Eq. (6) gives the following relation:

$$\theta_{Dn} = \theta_{Db}\left(1-\frac{N}{2n}\right)^{1/2} \quad \ldots(7)$$

The elastic moduli increase by increasing the cohesive energy[22]. Thus, using Eq. (3) the relation for elastic moduli can be written as:

$$B_n = B_b\left(1-\frac{N}{2n}\right) \quad \ldots(8)$$

and

$$Y_n = Y_b\left(1-\frac{N}{2n}\right) \quad \ldots(9)$$

where B_n, B_b and Y_n, Y_b are the bulk modulus and Young modulus of the nano crystalline and bulk material, respectively.

Recently, it is shown by Kholiya and Chandra[23] the quasi-harmonic approximation, i.e., the product of bulk modulus and the coefficient of volume thermal expansion as constant, is valid for nanomaterials therefore:

$$\alpha_n = \alpha_b\left(1-\frac{N}{2n}\right)^{-1} \quad \ldots(10)$$

The value of (N/2n) depends on the structure of the nanomaterial. For spherical nanosolids its value[18] may be given as:

$$\frac{N}{2n}=\frac{2d}{D} \quad \ldots(11)$$

where D is the diameter of spherical nanosolid and d is the diameter of the atom.

For nanowires:

$$\frac{N}{2n}=\frac{4d}{3L} \quad \ldots(12)$$

where L is the diameter of the nanowire.

3 Results and Discussion

The input parameters[14,17] required for the present work are given in Table 1. Eq. (4) is used for the calculation of melting temperature of Au nanowire and for spherical Pb nanosolid. The results are plotted in Figs (1 and 2), respectively along with the available experimental data[17]. While studying the size dependence of melting temperature, it is found that melting temperature increases on increasing the

Table 1 — Input parameters used in present work[14,17]

Sr. No.	Nanomaterials	α_{mb} (/K)	T_{mb} (K)	θ_{Db} (K)	Atomic size (nm)
1.	Au (nanowires)	8.7×10^{-5}		—	0.2884
2.	Pb (spherical nanosolid)	—	600.6	—	0.3898
3.	Fe (spherical nanosolid)	—	—	388	0.2482

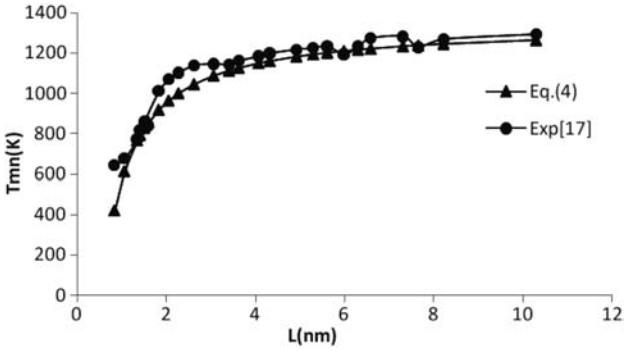

Fig. 1 — Size dependence of melting temperature of Au nanowire using Eq. (4)

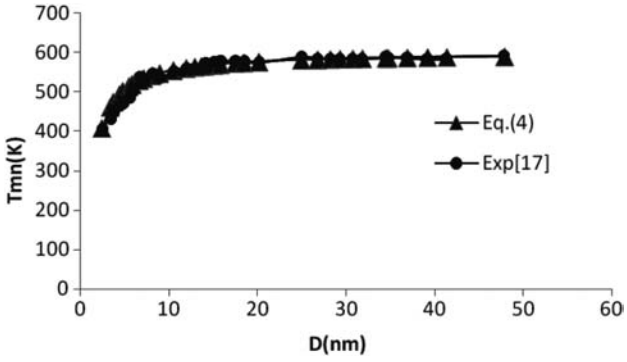

Fig. 2 — Size dependence of melting temperatute of Pb spherical nanosolid using Eq. (4)

diameter. A good agreement between theory and experiment encouraged the authors to extend the model to study the size dependence of Debye temperature. Eq. (7) is used to compute the size dependence Debye temperature of Fe and Pb spherical nanosolids. The computed values of Debye temperature for Fe and Pb spherical nanosolid are shown in Figs (3 and 4), along with the available experimental data[17]. There is a good agreement between theory and the available experimental data which demonstrates the suitability of the model presented for Debye temperature.

The elastic moduli increase by increasing the cohesive energy[22]. Thus, Eq. (3) may be extended to

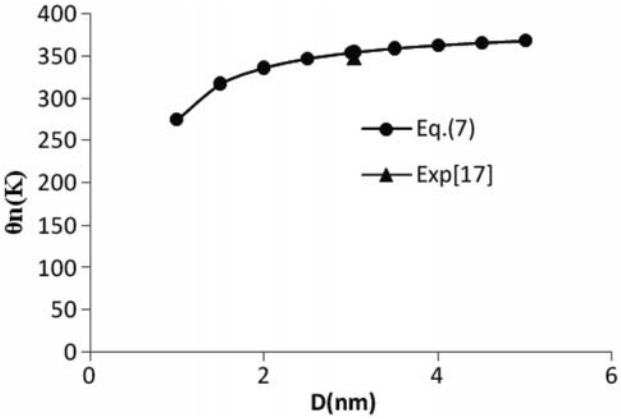

Fig. 3 — Size dependence of Debye temperature of Fe spherical nanosolid using Eq. (7)

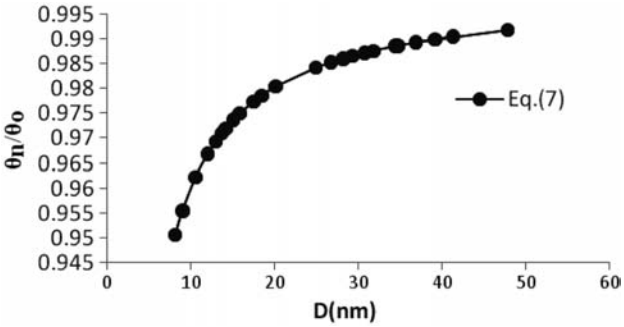

Fig.4 — Size dependence of θn/θo of Pb spherical nanosolid using Eq. (7)

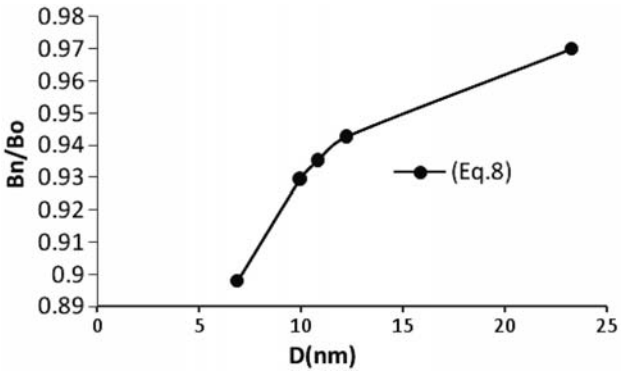

Fig. 5 — Size dependence of B_n/B_0 of Pb spherical nanosolid using Eq. (8)

calculate the size dependence of bulk modulus and Young modulus. Eqs (8 and 9) are used to compute the results of size dependence of bulk modulus and Young modulus of Pb spherical nanosolid and Au nanowire. The calculated values are plotted in Figs (5-7) along with the available experimental data. A good agreement is found between theory and

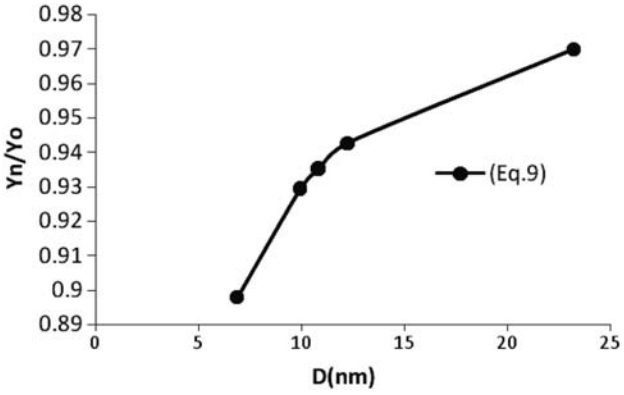

Fig. 6 — Size dependence of Y_n/Y_0 of Pb spherical nanosolid using Eq. (9)

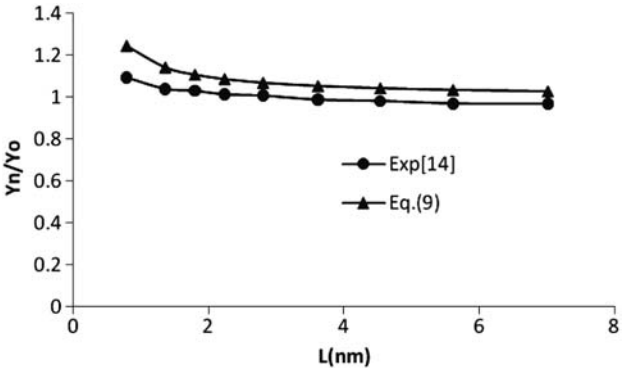

Fig. 7 — Size dependence of Y_n/Y_0 of Au nanowire using Eq. (9)

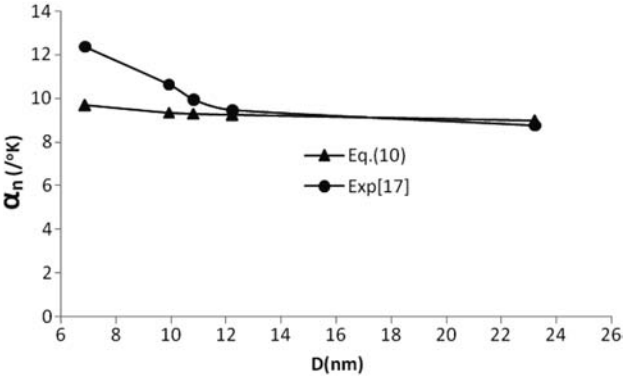

Fig. 8 — Size dependence of a_n of Pb spherical nanosolid using Eq. (10)

experimental data. The experimental studies on the Young modulus showed that it depends on the orientation[24,25], too. Present study reveals that Young modulus depends on orientation also. Two different orientations may be found using $\left(1\pm\frac{2d}{D}\right)$ for spherical nanosolids, and $\left(1\pm\frac{4d}{3L}\right)$ for nanowire. Since, the quasi-harmonic approximation, i.e., the product of bulk modulus and the coefficient of volume thermal expansion as constant, is valid for nanomaterials. The approximation is used for obtaining Eq. (10) to compute the size dependence of thermal expansion coefficient. The results are plotted along with available experimental data[17] and a good agreement is found between theory and experimental data. It is pertinent to mention here that although there are several experimental and theoretical studies[1-18] regarding the size dependent properties of nanomaterials but most of them are concerned only about any single property (cohesive energy or melting temperature or elastic modulus or Debye temperature) along with this some theoretical formulations require large computational work while the present study gives a simple and straightforward method to study the size dependence of most of the thermoelastic properties of nanomaterials like thermal expansion coefficient, Young modulus, bulk modulus, melting temperature and Debye temperature.

4 Conclusions

Simple theoretical method to study the size dependence of thermo elastic properties of nanosystems, has been presented. The results obtained are in good agreement with the available experimental data[14,17]. Due to the simple approach and applicability of the model, it may be of current interest to the researchers engaged in the study based on the size dependence of thermoelastic and thermodynamical properties of nanosystems, and may be extended to the variety of nanomaterials.

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