Size, shape and temperature effect on nanomaterials

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A simple theoretical model is developed to study the size, shape and temperature effect on nanomaterials. The temperature dependence of thermal expansion and Young modulus of different type (shape) of nanomaterials viz. spherical, nanowire and nanofilm has been studied. Size dependence of Young modulus in two different regions of temperatures viz. below Debye temperature and above Debye temperature has been investigated for different shape of nanomaterials. The thermal and elastic behaviour is related to vibrational frequency of nanomaterials. Therefore, the size dependence of vibrational frequency of different shape of nanomaterials has been computed. The model predictions are compared with the earlier theoretical and available experimental data. A good agreement supports the validity of the model proposed.

Keywords: Young Modulus, Thermal expansion, Vibrational frequency

1 Introduction

Nanomaterials are of current research interest due to their wide applications in science and technology. The stability of nanoscale devices is related to the elasticity and its temperature dependence. For example, the elastic instability induced by rising the temperature may cause the failure of integrated circuits as well as other microelectronic devices. In addition to this thermal stability of nanomaterial, is of both scientific and technological interest because in most of synthesis techniques, the nanomaterials are provided in powder form, which have to be consolidated to obtain dense material for potential applications. The thermal expansion is the fundamental property of nanomaterials which directly relates to applications. The experimental measurements show that the thermal expansion coefficients of nanocrystalline materials are larger than those of their polycrystalline counterparts which depend on temperature and influenced by the effect of size.

Lu and Sui\(^1\) reported that the average linear thermal expansion coefficients of nanocrystalline Ni-P increase with decrease of grain size. Zhang and Mitchell\(^2\) studied nanocrystalline Se and found the similar trend of variation. Yang \(et\) \(al\)\(^3\), studied the size dependent root mean square amplitude model. It has been discussed that model can predict \(\alpha_c\) (\(D = 40\) nm) value accurately in comparison with the experimental results, while a big divergence between them is found for \(\alpha_c\) (\(D = 16\) nm). Moreover, they concluded that \(\alpha_c\) (\(D\)) increases with decreasing \(D\). Xu \(et\) \(al\)\(^4\), studied the thermal expansion of as-prepared and annealed silver nanowires embedded in anodic lumina membrane with different diameters up to 800 K. For both as-prepared and annealed samples, the coefficients of thermal expansion have \(V\) shape change as the diameter increases and minimum values of the coefficient of thermal expansion do not correspond to the same diameters of nanowires. Zhao and Jiang\(^5\) extended the use of classical thermodynamics to nanoscale and studied the size effect on thermal properties of low dimensional materials. Kumar \(et\) \(al\)\(^6\), proposed a simple theoretical model for the size dependence of \(\alpha_c\) of nanomaterials. Thus, it seems that some efforts have been made to study \(\alpha_c\) with varying size or temperature. Moreover, a simple theoretical model, which includes the effect of size and temperature for different type (shape) of nanomaterials, has not yet been reported due to a difficult task. In the present paper, an effort has been made to achieve this task.

During thermal expansion, the elastic behaviour plays an important role. To understand elasticity, Young modulus is one of the important elastic constants. It is well known that when material dimensions approach nanoscale, a significant variation of mechanical properties can be observed comparing with their bulk counterpart owing to the high surface-to-volume ratio. Cuenot \(et\) \(al\)\(^7\), reported that the Young modulus of Ag and Pb nanowires...
increases dramatically with decreasing diameters. However, investigations on Cr and Si nanocantilevers showed that the moduli sharply decrease with decreasing diameter\textsuperscript{8,9}. On the other hand, the results reported by Wong \textit{et al}\textsuperscript{10} and Wu \textit{et al}\textsuperscript{11} showed that the moduli of SiC nanorod and Au nanowire are essentially independent of the diameter. Besides experimental investigations, theoretical analysis has also been employed to study the mechanical behaviour of nanomaterials, which includes the atomistic simulation as reviewed by Cao and Chen\textsuperscript{12}. Koh \textit{et al}\textsuperscript{13} reported that the Young modulus of Pt and Au nanowires increases with diameters until they approach to that of the bulk value. The size dependence of elastic properties has been found to be relevant to both the film surface crystallographic orientation and loading direction\textsuperscript{12,13}. The atomic structure analysis and energy calculations have been employed to identify the mechanism of the size dependent elastic properties, under different loading directions and surface orientations. Upon small axial deformation, the relationship between intralayer and interlayer bond length variation and film elastic stiffness has been established. It has been found that the atomic layers with larger bond length variation have higher elastic stiffness. Bhatt and Kumar\textsuperscript{14} proposed a simple theoretical model to study the size and orientation dependence of elasticity of nanowires and nanofilms. These authors\textsuperscript{14} studied the Young modulus of nanowire and nanofilms. The results obtained are compared with the available experimental data and computer simulation studies. The theory has been found to predict a good agreement with the experimental data. Thus, it seems that some theoretical as well as experimental efforts have been made to study the size and orientation dependence of Young modulus. Moreover, there is an urgent need to understand the effect of temperature and shape also. In the present work, we develop simple theoretical formulation is developed, which includes the effect of temperature and shape in addition to the size on different properties of nanomaterials.

2 Theoretical Formulation

To study the temperature dependence of thermal expansion of nanomaterials, Kumar \textit{et al}\textsuperscript{15} developed the following relation:

\[ \frac{\alpha}{\alpha_0} [1 - \alpha_n \delta_1 (T - T_0)]^{-1} \]  

where \( \alpha \) is the coefficient of volume thermal expansion, \( \delta_1 \) the Anderson-Grüneisen parameter, \( T \) the temperature and \( T_0 \) refers to their initial value. In Eq. (1), \( \alpha_0 \) is the initial value of volume thermal expansion of nanomaterials, which we write \( \alpha_n \) for simplicity. \( \alpha_n \) is the parameter, which depends on size and shape of nanomaterials and may be written as\textsuperscript{16}:

\[ \alpha_n = \alpha_0 \left(1 - \frac{N}{2n}\right)^{-1} \]

where \( \alpha_0 \) is the coefficient of volume thermal expansion of bulk material, \( N \) is the number of surface atoms and \( n \) is the total number of atoms of nanosolid. The surface atoms refer to the first layer of nanosolid. The values of \( N/2n \) depend on the size and shape of the nanomaterials. The method to find \( N/2n \) for different shape of nanomaterials has already been discussed by Qi\textsuperscript{17}. According to this model \( N/2n \) is 2d/D for spherical nanosolid with \( d \) as the diameter of atom and \( D \) the diameter of spherical nanosolid. For nanowire, \( N/2n \) is 4d/3L where \( L \) is the diameter of nanowire. For nanofilm, \( N/2n \) is 2d/3h, where \( h \) is the height (size) of nanofilm. Thus, we can write Eq. (1) for different type (shape) of nanomaterials:

Spherical nanosolid:

\[ \frac{\alpha}{\alpha_0} = \left[1 - \alpha_n \delta_1 \left(1 - \frac{2d}{D}\right)^{-1} (T - T_0)\right]^{-1} \]  

Nanowire:

\[ \frac{\alpha}{\alpha_0} = \left[1 - \alpha_n \delta_1 \left(1 - \frac{4d}{3L}\right) (T - T_0)\right]^{-1} \]

Nanofilm:

\[ \frac{\alpha}{\alpha_0} = \left[1 - \alpha_n \delta_1 \left(1 - \frac{2d}{3h}\right) (T - T_0)\right]^{-1} \]

Eqs (3-5) give the size and temperature dependence of the coefficient of volume thermal expansion of different type (shape) of nanomaterials.

To study elasticity, the Young modulus is one of the important elastic moduli. For nanomaterials, it has been discussed that thermal and elastic behaviour is inverse to each other\textsuperscript{16}. The temperature dependence of Young modulus is written as follows:
\[ \frac{Y}{Y_0} = [1 - \alpha_0 \delta_T (T - T_0)] \quad \ldots(6) \]

where \( \alpha_0 \) is size and shape dependent parameter as described above. Therefore, the relations of temperature dependence of Young modulus of different type (shape) of nanomaterials is written as follows:

Spherical nanosolid:

\[ \frac{Y}{Y_0} = \left[ 1 - \alpha_0 \delta_T \left( \frac{1 - \frac{2d}{D}}{T - T_0} \right)^{-1} \right]^{-1} \quad \ldots(7) \]

Nanowire:

\[ \frac{Y}{Y_0} = \left[ 1 - \alpha_0 \delta_T \left( \frac{1 - \frac{4d}{3L}}{T - T_0} \right)^{-1} \right]^{-1} \quad \ldots(8) \]

Nanofilm:

\[ \frac{Y}{Y_0} = \left[ 1 - \alpha_0 \delta_T \left( \frac{1 - \frac{2d}{3h}}{T - T_0} \right)^{-1} \right]^{-1} \quad \ldots(9) \]

Thus, the relations for different type (shape) of nanomaterials may be written as:

Spherical nanosolid:

\[ v_n = v_b \left( 1 - \frac{2d}{D} \right)^{-1/2} \quad \ldots(12) \]

Nanowire:

\[ v_n = v_b \left( 1 - \frac{4d}{3L} \right)^{-1/2} \quad \ldots(13) \]

Nanofilm:

\[ v_n = v_b \left( 1 - \frac{2d}{3h} \right)^{-1/2} \quad \ldots(14) \]

The elastic and vibrational characteristic of nanomaterials directly determines the stability and reliability of the devices. Therefore, in addition to the elasticity, it is very important to understand the vibrational mechanism of nanomaterials. For this purpose, Kumar et al. reported the following relation for size dependence of frequency:

\[ v_n = v_b \left( 1 - \frac{N}{2n} \right)^{1/2} \quad \ldots(10) \]

where \( v_n \) and \( v_b \) are vibrational frequency of nano and bulk materials. \( N/2n \) depends on size and shape of nanomaterials. Eq. (10) has been found to be quite satisfactory for the nanomaterials, which follow the Inverse Hall Petch Effect (IHPE). Actually, there are the nanomaterials for which bulk modulus decreases by decreasing the size viz. they become soft when size is decreased. On the other hand, there are the nanomaterials, which follow the Hall Petch Effect (HPE) viz. they become hard when size is decreased. Therefore, the size dependent of vibrational frequency for materials having HPE is written as:

\[ v_n = v_b \left( 1 - \frac{N}{2n} \right)^{-1/2} \quad \ldots(11) \]

3 Results and Discussion

The temperature dependence of the coefficient of thermal expansion and Young modulus for Cu nanofilm (2.2 nm) using Eqs (5) and (9) has been computed, respectively. The results obtained are shown in Fig. 1 along with the results reported by Liang et al. It should be mentioned that Liang et al. performed the molecular dynamics (MD) simulations of the biaxial tension of Cu thin films at different temperatures that were carried out to validate the temperature effect on the elastic modulus. The structures of Cu thin film with thickness 12 and 2.2 nm have been established with x, y and z being the [100], [010] and [001] directions, respectively.

Fig. 1 — Temperature dependence of \( a/a_0 \) using Eq. (5) and \( Y/Y_0 \) using Eq. (9) of Cu nanofilm (2.2 nm). • represent the results reported by Liang et al. using MD simulation.
The periodic boundary condition has been set in the x and y directions and z direction is free and embedded atom method potential is used. The simulations have been performed at the several temperatures in the range 300-800 K. The stress-strain curves and thus the biaxial modulus have been obtained at different temperatures. We have thus selected Cu nanofilm (2.2 nm) because of the fact that some results are available so that comparison can be made. The coefficient of volume thermal expansion is found to increase with increasing the temperature whilst Young modulus decreases with increasing temperature. Our computed results are found to present to a good agreement with the available data\textsuperscript{19}. To include the effect of shape we have included spherical nanosolid and nanowire also and compared the results. Eqs (3-5) are used to study \(\alpha/\alpha_0\) and Eqs (7-9) for \(Y/Y_0\) to compute their temperature dependence. The results obtained are shown in Fig. 2. It is found that \(\alpha/\alpha_0\) increases with increasing the temperature for all type of nanomaterials considered in the present work viz. spherical, nanowire and nanofilm of Cu (2.2 nm). Moreover, the value of \(\alpha/\alpha_0\) is found to decrease from spherical to nanowire and nanofilm. On the other hand, Young modulus is found to decrease by increasing the temperature. For different shape, the reverse effect is found as observed in the \(\alpha/\alpha_0\). To confirm the model predictions we have also included the effect of size and repeated our computational work for Cu (12 nm). The results obtained for the temperature dependence of \(\alpha/\alpha_0\) and \(Y/Y_0\) are shown in Figs 3 and 4 along with the results reported by Liang \textit{et al}\textsuperscript{19}, which are available for temperature dependence of \(Y/Y_0\) of Cu (12 nm) nanofilm. These are shown in Fig. 3. It is found that model predictions are in good agreement with the results reported by Liang \textit{et al}\textsuperscript{19}. A comparative study is shown in Fig. 4. A similar trend as obtained in Cu (2.2 nm), is observed. However, the model predicts that increasing the size, the shape has less effect. To confirm the model predictions, the application of our model is extended by changing the material. For this purpose, we have selected Si (2.2 and 10.9 nm) because of the availability of MD simulation results\textsuperscript{19} so that model predictions may be judged. The results are shown in Figs 5-8. The model is found to give the similar trends in good agreement with the available MD simulation results\textsuperscript{19}. The origin of size and temperature dependent of Young modulus has been studied by Ao \textit{et al}\textsuperscript{20} by considering the size effects on surface bond contraction and melting temperature variation. The results show that Young modulus decreases with a shrinking disparity between melting temperature and materials application temperature, while surface bond...
Thus, the effect of size including the effect of temperature is an interesting and important property of nanomaterials. In the present paper, the application of our model is extended to compute the size dependent of Young modulus at different temperature. Two different regions have been investigated viz. when the application temperature is more than the Debye temperature ($T_D$) and less than $T_D$. We have selected different nanowires because of the fact that some earlier results\cite{20,21} are available so that the model predictions may be compared. In addition to this, the effect of shape is also included (spherical nanosolid and nanofilm). We used Eqs (7-9) is used to study the size and shape dependent of Cu, Ag, Au and Al. In Eqs (7-9), $T_0$ is the reference temperature viz. Debye temperature of the material is considered. In the present paper, the size and shape dependent of Young modulus are computed at two temperatures viz. the temperature which is less than the Debye temperature, and higher than the Debye temperature. At the temperature less than Debye temperature, Young modulus is found to increase by decreasing the size of nanomaterial. Moreover, a reverse trend is found at the temperature greater than the Debye temperature. The results obtained for Cu are shown in Figs 9 and 10. At $T = 0$ K, the theoretical results reported by Ao et al\cite{20}, for comparison purpose, are included. Our results show the similar trend of variation as reported by Ao et al\cite{20}. At $T=300$ K, our model predictions are compared with the simulation results\cite{21}. It is observed that our results are found to be in good agreement with the computer simulation studies\cite{21} and earlier theoretical predictions. It is very interesting and important to mention here that present model is very simple as compared with earlier investigations\cite{20,21} and gives good results. To demonstrate the
Fig. 9 — Size dependence of $\frac{Y}{Y_0}$ using Eqs (7-9) of Cu at $T = 0K$, • represent the results reported by Ao et al\textsuperscript{20} using theoretical model for nanowire

Fig. 10 — Size dependence of $\frac{Y}{Y_0}$ using Eqs (7-9) of Cu at $T = 300 K$, • represent the simulation results reported by Liang and Upmanyu\textsuperscript{21} for nanowire

Fig. 11 — Size dependence of $\frac{Y}{Y_0}$ using Eqs (7-9) of Ag at $T = 0K$

applicability of the model, we have repeated our computational work to some other nanomaterials viz. Ag, Au and Al. A similar trend of variation is found. The results obtained are shown in Figs 11-16.

For the stability and reliability of nanomaterial devices, it is very important and interesting to understand the vibrational mechanism. The size dependent of vibrational frequency of different type (shape) of nanomaterials has been studied. We have considered Si, Cu and Ag for this purpose because of the fact that the model predictions may be compared. Eqs (12-14) are used to compute the size dependence of vibrational
Fig. 15 — Size dependence of $Y/Y_0$ using Eqs (7-9) of Al at $T = 0$ K

Fig. 16 — Size dependence of $Y/Y_0$ using Eqs (7-9) of Al at $T = 500$ K

Fig. 17 — Size dependent of $v/v_b$ of Si using Eqs (12-14), • represent results based on phonon dispersion relation $^{22}$ and * represent results based on lattice strain and binding energy change $^{23}$ for nanofilm

Fig. 18 — Size dependent of $v/v_b$ of Cu using Eqs (12-14), • represent MD simulation results $^{24}$ and * represent experimental data $^{25}$

Fig. 19 — Size dependent of $v/v_b$ of Ag using Eqs (12-14), • represent the results reported by Liang et al. $^{23}$ using theoretical model These results are included in Fig. 17 for comparison purpose. Our model predictions are in good agreement with these results. In addition to this, the results for spherical nanosolid and nanowire are also reported. There are similar trend of variations. It is observed that frequency increases from nanofilm to nanowire and spherical. The similar trend of variation is found in other solids viz. Cu and Ag with good agreement as compared with earlier theoretical and experimental results $^{23-25}$.

The present model is very simple and straightforward, which contained less input parameters as compared with earlier models. We have also presented our results for the materials for which experimental data are not available. This may help the researchers engaged in the experimental study. Due to the simplicity and applicability, the model may be useful for other nanomaterials of current interest.

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