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Original Research Article

Development of size and shape dependent model for vibrational frequency of nanocrystals

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ABSTRACT
The characteristics of bulk materials depend on their structure. But at nanoscale size and shape of the materials are the important factor. High surface to volume ratio is the most important property of materials. Thermodynamic properties of the materials have been affected by this high surface to volume ratio. Bulk and nanomaterials have different properties. The reliable theoretical framework about the elastic modulus's size influence and vibrational. In order to direct the application of nanomaterials, frequency is important. The structure of metal nanoparticles is shown by their vibrational spectra and the low temperature behavior of the thermal characteristics has been ascertained by analyzing the vibrational spectra of metal nanoparticles. Vibration is actually a mechanical phenomena. Mechanical system vibrates at one or more of its natural frequency. Vibrational frequency has been used many years to identify bonding arrangement of molecules. Since every bond has a unique frequency, molecular structure may be inferred from vibrational frequency. In the current paper, we will develop a simple theoretical model to understand the variation of vibrational frequency of nanomaterials with size. We also include the shape factor in present study. We will study size and shape dependence of vibrational frequency for different nanomaterials. We will also compare our theoretical results with suitable experimental data. Our theoretical findings will match the existing experimental data rather well, indicating the validity of the suggested model.

1. Introduction

The characteristics of bulk materials depend on their structure. But at nanoscale size and shape of the materials are the important factor. High surface to volume ratio is the most important property of materials. Thermodynamic properties of the materials have been affected by this high surface to volume ratio. Energy band gap increases with increase in size of nanocrystals while vibrational frequency decreases with increase in the size of nanocrystals. Dielectric constant is also decreases with increase in the size [1]. Bulk and nanomaterials have different properties. A precise theoretical model should direct the utilization of nanomaterials about the size influence of vibrational frequency and elastic modulus. [2]. The structure of metal nanoparticles is shown by their vibrational spectra and vibrational spectra of metal nanoparticles has been used to determine the function of thermal properties at low temperature. The theoretical study on size evolution of vibrational spectra has been studied [3]. Simple theoretical model has been investigated the relationship between thermodynamic and vibrational properties of nanoparticles on size and form [4]. The dependence of vibrational and thermodynamic parameters of nanoparticles on size and form has been studied [5].

Vibration is actually a mechanical phenomena. Mechanical system vibrates at one or more of its natural frequency. Vibrational frequency has been used many years to identify bonding arrangement of molecules. Since every bond has a unique frequency, molecular structural information may be obtained from vibrational frequency. In the current paper, we develop a simple theoretical model to understand the change of vibrational frequency of nanomaterials with size of materials. In the current work, we will develop the unique model for size and shape dependence of vibrational frequency of nanomaterials with suitable experimental data.

2. Theoretical formulations

Cohesive energy of nanomaterials may be read as follows [6]:

$$E_{cn} = E_0\left(1 - \frac{3N}{4n}\right) \quad (1)$$

where E_0 is the cohesive energy of bulk material and total number of atoms in nanomaterials is n and number of surface atoms is N.

The square root of cohesive energy is exactly related to the electron vibration frequency in a solid atom. So, vibrational frequency of nanomaterials and vibrational frequency of electrons in atoms of bulk material can be expressed as follows [7]:

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$$\frac{\omega_n}{\omega_b} = \left(\frac{E_{cn}}{E_0}\right)^{1/2} \quad (2)$$

where ω_n is the vibrational frequency of nanomaterials and ω_b is the vibrational frequency of bulk materials.

Using Eq. (1) and (2) vibrational frequency can be written as:

$$\frac{\omega_n}{\omega_b} = \left(1 - \frac{3N}{4n}\right)^{1/2} \quad (3)$$

Bhatt and Kumar [8] provided the detail discussion of Qi model [6]. Mathematical form of model can be written as follows:

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

where T_{mn} is the melting temperature of nanomaterials and T_{mb} is the melting temperature of bulk materials. k is the dimensionless parameter which can have different values [8].

It has been discussed that melting temperature is related to cohesive energy by the following relation [9, 10].

$$\frac{E_n}{E_b} = \frac{T_{mn}}{T_{mb}} \quad (5)$$

Eq. (2) can be now written as according to Eq. (4) and Eq. (5) as:

$$\frac{\omega_n}{\omega_b} = \left(1 - \frac{N}{2n}\right)^{k/2} \quad (6)$$

Eq. (6) can be written for different shapes as follows (Table 1):

Film

$$\frac{\omega_n}{\omega_b} = \left(1 - \frac{0.665d}{h}\right)^{k/2} \quad (7)$$

Dodecahedral

$$\frac{\omega_n}{\omega_b} = \left(1 - \frac{0.898d}{a}\right)^{k/2} \quad (8)$$

Icosahedral

$$\frac{\omega_n}{\omega_b} = \left(1 - \frac{1.323d}{a}\right)^{k/2} \quad (9)$$

Wire

$$\frac{\omega_n}{\omega_b} = \left(1 - \frac{1.333d}{L}\right)^{k/2} \quad (10)$$

Spherical

$$\frac{\omega_n}{\omega_b} = \left(1 - \frac{2d}{D}\right)^{k/2} \quad (11)$$

Hexahedral

$$\frac{\omega_n}{\omega_b} = \left(1 - \frac{2d}{a}\right)^{k/2} \quad (12)$$

Octahedral

$$\frac{\omega_n}{\omega_b} = \left(1 - \frac{2.449d}{a}\right)^{k/2} \quad (13)$$

Tetrahedral

$$\frac{\omega_n}{\omega_b} = \left(1 - \frac{4.898d}{a}\right)^{k/2} \quad (14)$$

In the present paper, we have used Eqs. (7) to (14) to calculate the vibrational frequency of different materials for different shapes.

Table 1: Values of *N/n* for different shapes [8].

Shape	*N/n*
Film	1.33 *d/h*
Dodecahedral	1.796 *d/a*
Icosahedral	2.646 *d/a*
Wire	2.666 *d/L*
Spherical	4 *d/D*
Hexahedral	4 *d/a*
Octahedral	4.898 *d/a*
Tetrahedral	9.797 *d/a*

3. Results and discussion

In the current paper, we obtained the Eq. (6) after extension of the model [6]. This model explains the variation of vibrational frequency of nanomaterials with size for different shapes. We selected different materials viz. ZnO, Si, CdS, InP. In the present paper, we used Eq. (6) to compute the relative vibrational frequency at different sizes for different shapes. Variation of relative vibrational frequency with size and shape is given in the Figure 1.

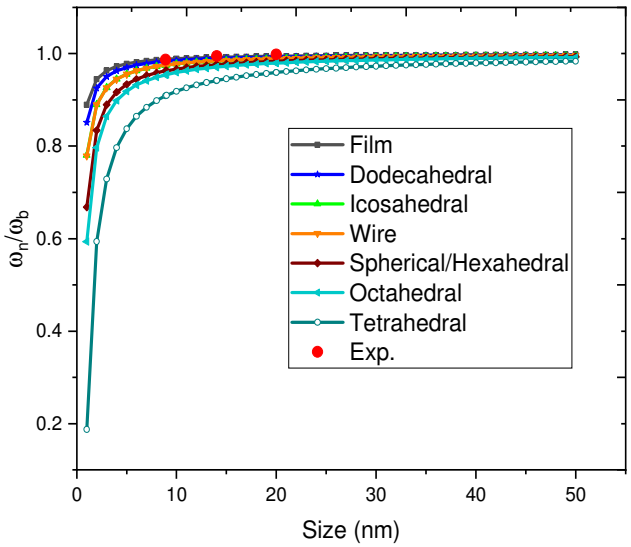

Figure 1: Size and Shape dependence of relative vibrational frequency for ZnO (Spherical) for k=2 using Eq. (11). ● shows the experimental data [11].

Figure 1 shows how vibrational frequency vary with size for k = 2 for different shapes along with the available experimental data [11]. Variation in relative vibrational frequency increases with size. Shift in this variation is greater for film and lower for tetrahedral. Our theoretical findings fit well with the experimental data that is available [11].

Figure 2 shows the change of relative vibrational frequency with size for different shapes for Si for k = 2 along with the available experimental data [12].

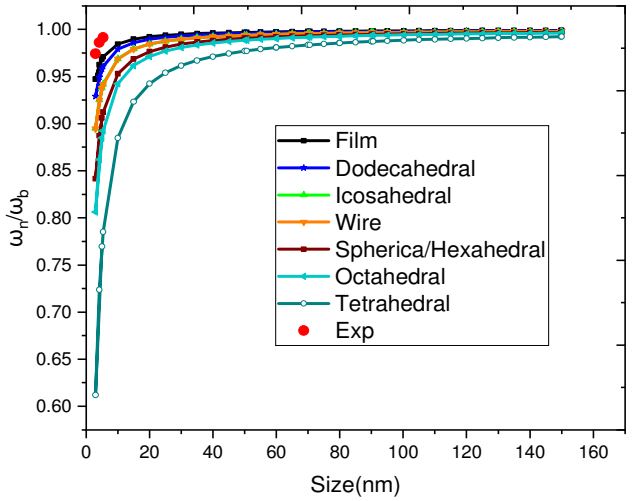

Figure 2: Size and Shape dependence of relative vibrational frequency for Si (Film) for k = 2 using Eq. (7).

Figure 3 and Figure 4 shows the variation in relative vibrational frequency for CdS and InP with size and shape. We have lack of experimental data in these cases. Experimental data proves the validity of our model.

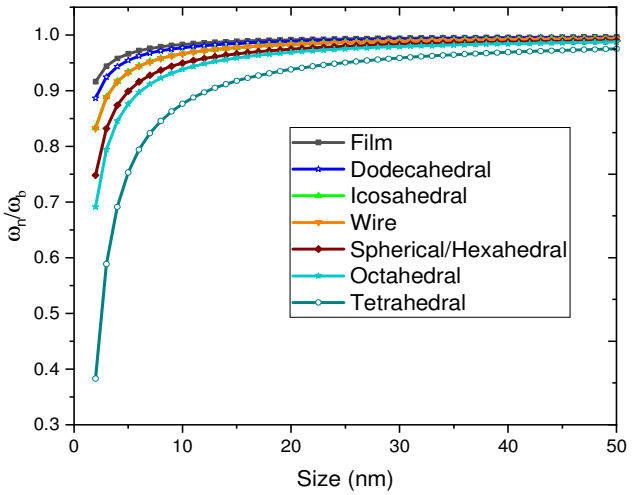

Figure 3: Size and Shape dependence of relative vibrational frequency for CdS for k = 2 using Eqs. (7) to (14).

4. Conclusions

In light of the experimental findings, it is inferred that, a simple theoretical model has been created to examine the size and shape dependency of nanomaterials' vibrational frequency. The present theoretical results on ZnO, Si nanomaterials are consistent with available experimental data. It demonstrates the model's validity. Also, we have studied shape dependence on vibrational frequency of CdS and InP nanomaterials.

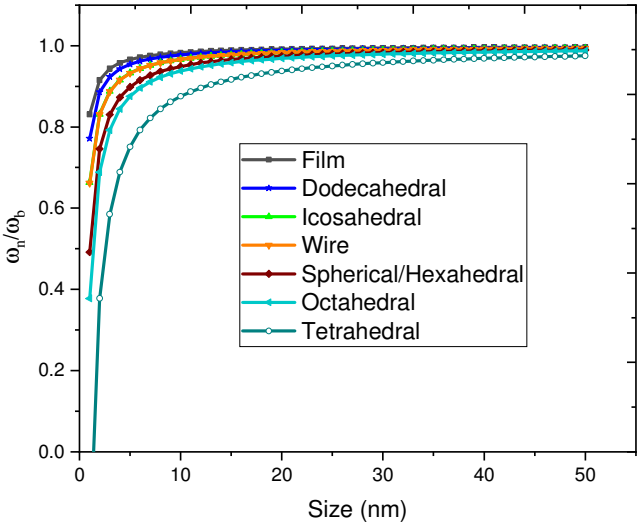

Figure 4: Size and shape dependence of relative vibrational frequency for InP for k = 2 using Eqs. (7) to (14).

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