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Impact of size and temperature on thermal expansion of nanomaterials

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Abstract. A theoretical method has been discussed to study the size dependency of thermal expansion of nanomaterials at higher temperature by considering the surface effect. A thermodynamical analysis of the equation of state (EoS) is studied from the knowledge of thermal expansion of nanomaterials based on theoretical thermodynamical relations. It is observed that thermal expansion coefficient increases with decrease in grain size whereas, V/V_0 increases with increase in temperature for nanomaterials of different grain sizes. We have studied the size and temperature dependence of thermal expansion of Cu, Ag, Ni, Sn, Se and Zn nanomaterials in different shapes (spherical, nanowire and nanofilm). The available experimental data confirm these theoretical predictions that demonstrate the validity of our work.

Keywords. Equation of state; size effect; nanomaterials; thermal expansion.

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1. Introduction

It is believed that nanomaterials are to be the soul of the next technological development in all spheres of science. Nanomaterials differ significantly from their bulk counterparts primarily because of their small size. Various physical properties such as hardness, melting temperature, elastic modulus, sintering ability and electronic structure may depend on grain size. Nanomaterials, nanoparticles, nanowires and nanotubes have been reported [1–3] to show physical, chemical and mechanical properties that are markedly different from their corresponding bulk counterparts. Size-dependent elastic modulus and melting point of Au and Ag at nanosize have been studied [4] and it is observed that reduction in particle size brings about a change in their properties. Theoretical consideration of the observed size dependence of the lattice strain, elastic modulus and melting point for Ag and Au nanostructures can be understood [5] by the theory of under-coordination, which not only verifies the theoretical expectation but also provides criteria for nanoscale

materials. The thermal expansion coefficients of Cu nanowire and its bulk were investigated [6] using theoretical equations based on thermodynamical relations in the temperature range upto 900 K. Both the size and crystal orientation effects on the thermal expansion coefficients of nanowires were studied [6] and it was noticed that the volume thermal expansion of Cu nanomaterial is three times its linear thermal expansion irrespective of the crystal orientations. Also, theoretical equations based on thermodynamical relations to study the thermomechanical properties of copper nanofilm is investigated by Gan and Chen [7] at different temperatures and the temperature softening effect on the film strength and modulus is observed. Thermal expansion coefficient of Zn nanowire was measured [8] using the *in-situ* high resolution X-ray diffraction technique and a significantly large lattice expansion with reduction in grain size was observed. Qi [9] calculated the size-dependent melting temperature of Pb, Sn and In nanoparticles using the theory that the cohesive energy of the nanosolids is the sum of the interior and the surface atoms and it was shown that the melting temperature of the nanosolids decreases with decrease in grain size.

It is very much evident from the above discussion that numerous experimental studies have been performed to study the impact of size and temperature on nanomaterials. However, the theoretical efforts are very few.

In this paper, we present a simple theoretical approach to study the expansion behaviour of nanomaterials under the effect of grain size and temperature. An equation of state (EoS) is derived and it has been used to calculate V/V_0 for Cu, Ag, Ni, Sn, Se and Zn nanosolids, viz., spherical nanosolids, nanowires and nanofilms with free surface. Moreover, the validity of the method is verified by the available experimental data.

2. Method of analysis

The Anderson Gruneisen parameter [10] is given by

$$\delta_T = -\frac{1}{\alpha B_T}\left(\frac{\partial B_T}{\partial T}\right)_P = \frac{V}{\alpha}\left(\frac{\partial \alpha}{\partial V}\right)_P, \tag{1}$$

and bulk modulus reads as

$$B_T = -V\left(\frac{\partial P}{\partial V}\right)_T. \tag{2}$$

Using the Maxwell thermodynamics relation given by Wallace [11] we have

$$B_T\left(\frac{\partial \alpha}{\partial P}\right)_T = \frac{1}{B_T}\left(\frac{\partial B_T}{\partial T}\right)_P. \tag{3}$$

From eqs (2) and (3), Anderson parameter can also be defined as

$$\delta_T = \frac{V}{\alpha}\left(\frac{\partial \alpha}{\partial V}\right)_P. \tag{4}$$

On integration, eq. (4) gives

$$\frac{\alpha}{\alpha_0} = \left(\frac{V}{V_0}\right)^{\delta_T}, \tag{5}$$

where α_0 and V_0 are thermal expansion coefficient and volume at room temperature and atmospheric pressure, respectively. Equation (5) reads [12] as

$$\frac{\alpha}{\alpha_0} = \left(\frac{r}{r_0}\right)^{3\delta_T}. \tag{6}$$

Kumar [13] derived the relation for $r(T)$ as a function of temperature by considering the definition of thermal expansion coefficients as

$$\alpha = \frac{1}{V}\left(\frac{\mathrm{d}V}{\mathrm{d}T}\right). \tag{7}$$

On solving we get

$$\frac{\mathrm{d}r}{\mathrm{d}T} = \frac{\alpha r}{3}. \tag{8}$$

As $V \propto r^3$, from eqs (7) and (8), we get

$$\frac{\mathrm{d}r}{\mathrm{d}T} = \frac{\alpha_0}{3}\left(\frac{r^{3\delta_T+1}}{r_0^{3\delta_T}}\right). \tag{9}$$

Integration of eq. (9) gives

$$r(T) = r_0\left(\frac{1}{1-\delta_T\alpha_0(T-T_0)}\right)^{1/3\delta_T}. \tag{10}$$

Now from eqs (10) and (7), the expression for thermal expansion coefficient is

$$\alpha(T) = \alpha_0\left(\frac{1}{1-\delta_T\alpha_0(T-T_0)}\right). \tag{11}$$

From eqs (6) and (11), we can derive

$$V = V_0\left(\frac{1}{1-\delta_T\alpha_0(T-T_0)}\right)^{1/\delta_T}, \tag{12}$$

where V, T and subscript 0 are the volume, temperature and the reference value of parameters, respectively.

Using molecular dynamics simulation, Prakash [14] determined α of a single-walled carbon nanotubes (CNT) and used the temperature dependence of α as

$$\alpha = a + bT + cT^2. \tag{13}$$

One can write eq. (13) to satisfy the initial boundary condition as follows:

$$\alpha = a + b(T-T_0) + c(T-T_0)^2$$

or

$$\alpha = \alpha_0 + \alpha_0'(T-T_0) + \alpha_0''(T-T_0)^2. \tag{14}$$

The first- and second-order derivatives of α with T are defined by α' and α''. It is possible to define α_0' and α_0'' in terms of α_0, which reads as follows [15]:

$$\alpha_0' = \alpha_0^2\delta_T$$

and

$$\alpha_0'' = \alpha_0^3 \delta_T^2.$$

So, eq. (14) is written as

$$\alpha = \alpha_0 + \alpha_0^2 \delta_T (T - T_0) + \alpha_0^3 \delta_T^2 (T - T_0)^2. \tag{15}$$

In fact eq. (15) is an incomplete equation in which higher-order terms are excluded. On including all the higher-order terms in eq. (15), it becomes

$$\alpha = \alpha_0 + \alpha_0^2 \delta_T (T - T_0) + \alpha_0^3 \delta_T^2 (T - T_0)^2 + \alpha_0^4 \delta_T^3 (T - T)^3 + \cdots$$

or

$$\frac{\alpha}{\alpha_0} = \{1 - \alpha_0 \delta_T (T - T_0)\}^{-1}. \tag{16}$$

Using the definition of α, the integration of eq. (16) gives

$$V = V_0 \left(\frac{1}{1 - \delta_T \alpha_0 (T - T_0)} \right)^{1/\delta_T}, \tag{17}$$

where α_0 is the reference value of the coefficient of thermal expansion. For simplicity, we can write this as α_p, which is a size- and shape-dependent parameter. Equation (17) is the same as eq. (12), which justifies the validity of the theory used. Kumar and Kumar [16] derived the relation for α_p based on eqs (1)–(3) and thermodynamics relations as follows:

$$\alpha_p = \alpha_b \left(1 - \frac{N}{2n} \right)^{-1}, \tag{18}$$

where N is the total number of surface atoms and n is the total number of nanosolids. α_b is the coefficient of volume thermal expansion of the bulk material. The surface atoms refer to the first layer of the nanosolid. Qi [9] discussed the method to find $N/2n$ for different shapes of nanomaterials and the expressions of $N/2n$ have been tabulated in table 1, where D is the diameter of a spherical nanosolid, d is the diameter of the atom, l is the length of nanowire and h is the height of nanofilm.

Using the values of $N/2n$ from table 1 in eqs (17) and (18), the expressions for V/V_0 for different shapes and sizes of nanosolids become

$$\frac{V}{V_0} = \left(\frac{1}{1 - \delta_T \alpha_b \left(1 - \frac{2d}{D}\right)^{-1} (T - T_0)} \right)^{1/\delta_T}, \tag{19}$$

Table 1. $N/2n$ for different nanosolids [9].

Nanomaterials	$N/2n$
Spherical nanosolids	$2d/D$
Nanowires	$4d/3l$
Nanofilms	$2d/3h$

$$\frac{V}{V_0} = \left(\frac{1}{1 - \delta_T \alpha_b \left(1 - \frac{4d}{3l}\right)^{-1} (T - T_0)} \right)^{1/\delta_T}, \tag{20}$$

$$\frac{V}{V_0} = \left(\frac{1}{1 - \delta_T \alpha_b \left(1 - \frac{2d}{3h}\right)^{-1} (T - T_0)} \right)^{1/\delta_T}. \tag{21}$$

Equations (19)–(21) are the expressions for V/V_0 for spherical nanosolids, nanowires and nanofilms, respectively. In this paper, we use eqs (19)–(21) to study the temperature- and size-dependent V/V_0 for different nanomaterials. Throughout the calculation, the value of δ_T is taken to be 4 as discussed by Kumar and Kumar [19].

3. Results and discussion

In order to analyse eq. (18) [16], we have calculated the size-dependent thermal expansion coefficient of Se for different shapes of nanomaterial (spherical, nanowire and nanofilm) with increasing grain size. The theoretical results obtained are reported in figure 1 along with the available experimental data. Input parameters used for calculations are listed in tables 1 [9] and 2 [8,17,18].

The theoretical results obtained by eq. (18) for Se nanosolid for spherical shape is compared in figure 1 along with the available experimental data [20]. It is seen that the thermal expansion coefficient increases with decreasing grain size, which supports the validity of eq. (18). Size effect is also realized in Se nanowire and nanofilm and drift is more or less the same as in spherical nanomaterials.

The grain size dependence of V/V_0 for Cu, Ag, Ni, Sn, Se and Zn nanomaterials have been calculated from eqs (19)–(21) from room temperature to higher temperatures. A positive V/V_0 is noted in all nanomaterials for different shapes (spherical, nanowire and nanofilm), which may be understood by the effects of anharmonic lattice potential on the equilibrium lattice separations and characterized by the Gruneisen parameter [21]. The results are reported in figures 2–9 along with the available experimental data. V/V_0 of Cu nanomaterial in different grain sizes for spherical nanosolid, nanowire and nanofilm with increasing temperature are shown in figures 2 and 3. It is observed that V/V_0 increases with decreasing grain size from 20 to 10 nm for spherical

Table 2. Values of input parameters used in calculations [8,17,18].

Nanomaterials	α_b (10^{-5} K^{-1})	d (nm)
Cu	0.62	0.2556
Ag	1.8	0.219
Ni	3.3	0.248
Sn	2.2	0.372
Se	9.45	0.437
Zn	0.54	0.495

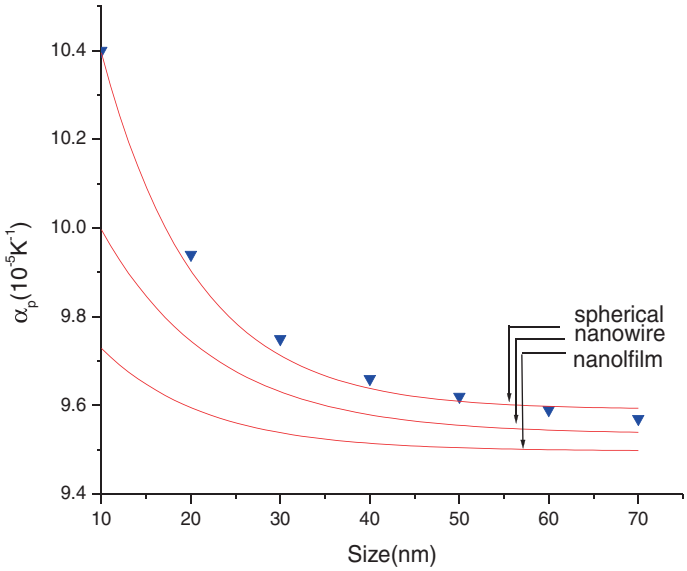

Figure 1. Size-dependent thermal expansion coefficient of Se using eq. (18). Experimental data [20] are shown by ▼ for spherical nanosolid.

nanosolid, nanowire and nanofilm. It is noted that the difference in V/V_0 is small in nanofilm but spherical particles show a large difference at higher temperatures. Figures 4 and 5 predict the size-dependent V/V_0 of Se (10 nm) and (20 nm) nanomaterials from temperatures 300 to 1000 K for different shapes, viz., spherical nanosolid, nanowire and

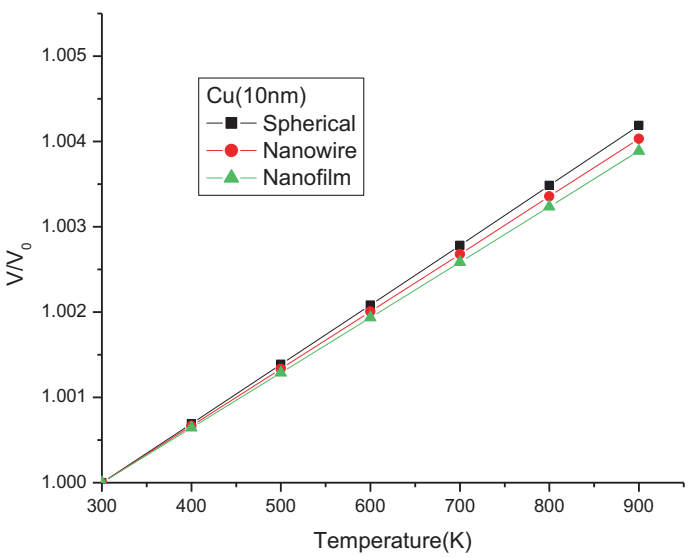

Figure 2. Temperature dependence of V/V_0 of Cu (10 nm) using eqs (19)–(21).

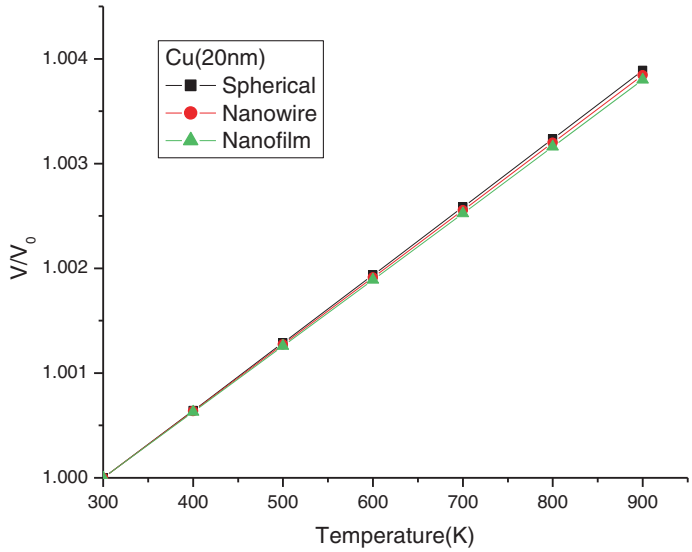

Figure 3. Temperature dependence of V/V_0 of Cu (20 nm) using eqs (19)–(21).

nanofilm. It is clear from the plots that as the grain size decreases with increase in temperature, V/V_0 increases. From figures 4 and 5, it is evident that as the shape changes from spherical nanosolid to nanowire to nanofilm, the impact of size decreases. It is noted from the graphs that in Se, the difference in V/V_0 is maximum at higher temperatures whereas for Cu it is small. This is obvious as the bulk thermal expansion of Se is very high.

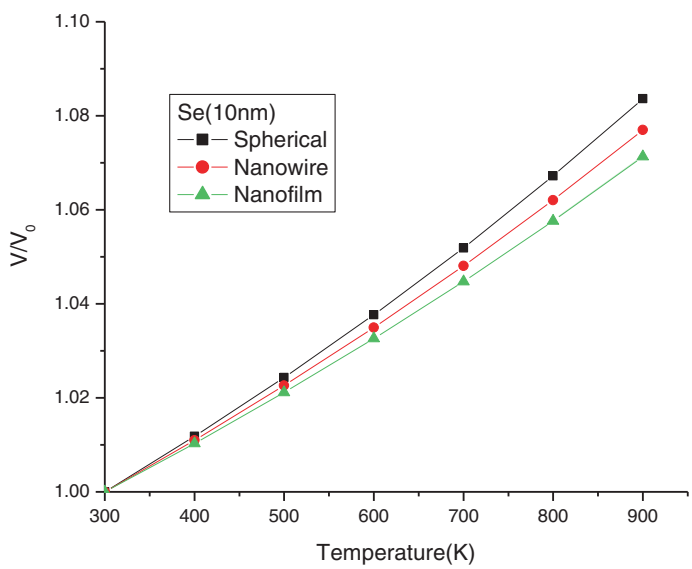

Figure 4. Temperature dependence of V/V_0 of Se (10 nm) using eqs (19)–(21).

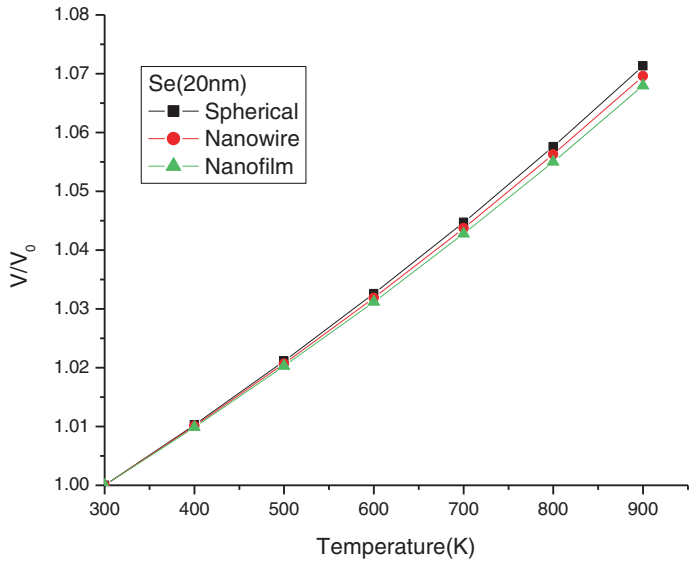

Figure 5. Temperature dependence of V/V_0 of Se (20 nm) using eqs (19)–(21).

Experimentally, thermal expansion coefficient of Zn (40 nm) nanowires was measured [8] by high-resolution XRD with temperature. Using eq. (20), V/V_0 was calculated for Zn nanowire (40 nm) and it is reported in figure 6 along with the available experimental data [8]. It is observed from the figure that upto a temperature of about 500 K, our results

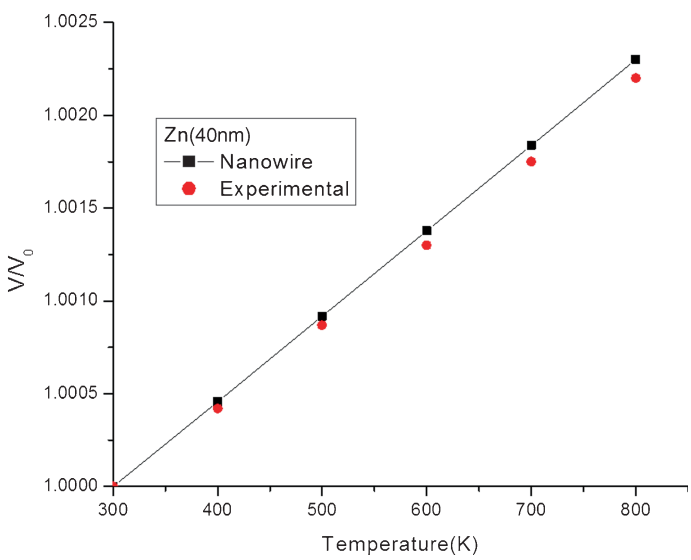

Figure 6. Temperature dependence of V/V_0 of Zn (40 nm) using eq. (20). Experimental data [8] are shown by solid circles.

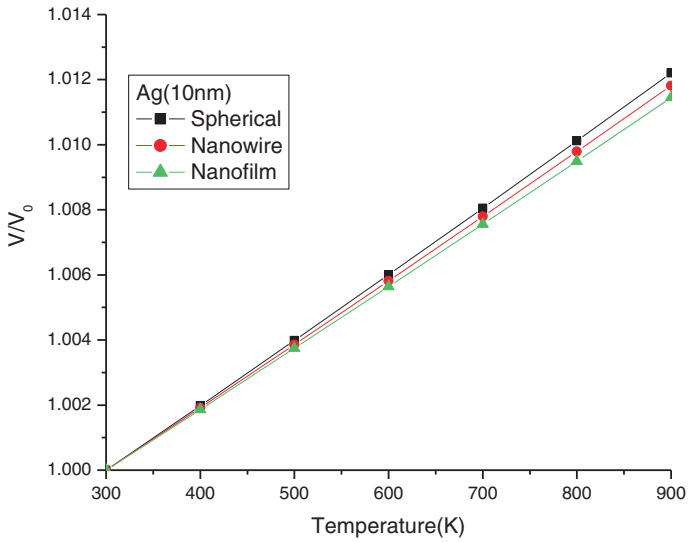

Figure 7. Temperature dependence of V/V_0 of Ag (10 nm) using eqs (19)–(21).

are very close to the experimental data. Beyond 500 K, there is a slight change with the experimental data. This difference may be due to the fact that the nanoparticles are considered as ideal spheres and the shape difference between spherical and non-spherical particles has not been studied. The theoretical predictions for Cu, Ag and Sn nanomaterials for different shapes (spherical nanosolid, nanowire, nanofilm) are presented in figures 7–9.

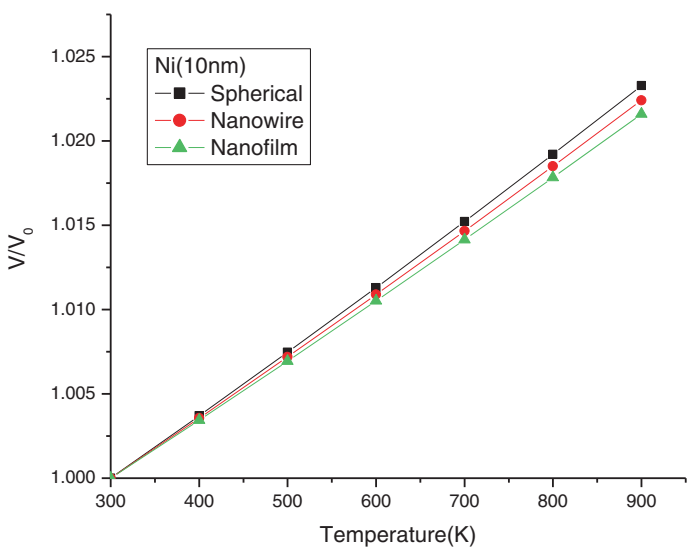

Figure 8. Temperature dependence of V/V_0 of Ni (10 nm) using eqs (19)–(21).

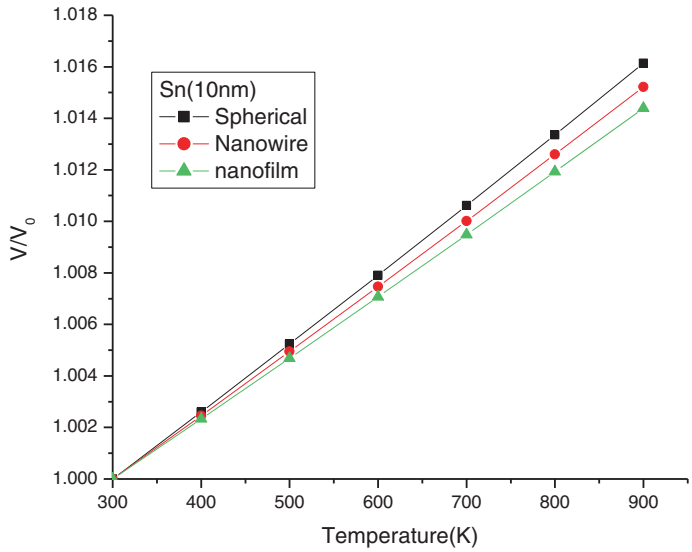

Figure 9. Temperature dependence of V/V_0 of Sn (10 nm) using eqs (19)–(21).

Qi [9] has found that the cohesive energy of the nanoparticle decreases as the particle size increases. This shows the inconsistency of nanomaterials in comparison to their bulk counterparts. This is because the surface to volume ratio increases, as the grain size decreases. If we compare $N/2n$ for spherical to nanowire to nanofilm, the ratio turns out to be 3:2:1. Therefore, the V/V_0 variation for spherical nanoparticle, nanowire and nanofilm of the same grain size is 3:2:1.

Consequently, V/V_0 increases with decrease in grain size and increase in temperature. It should be noted from eqs (19)–(21) that the initial size d of the atom also influences the value of V/V_0, which increases on increasing the initial size of the atom.

4. Conclusion

In this paper thermal expansion of nanosolids, viz., spherical nanosolids, nanowires and nanofilms, has been calculated by considering the surface effect. A simple theoretical method was discussed to calculate V/V_0 for spherical nanosolids, nanowires and nanofilms. It is reported from the theory that the thermal expansion increases with decreasing grain size. This theory is useful for finding thermal expansion of those nanomaterials where experimental data are not found so far.

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