Shape- and dimension-dependent study of volume thermal expansion of nanomaterials**

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Nanomaterials are the foundation of nanotechnology and they exist in different dimensions, shapes and sizes in nature. A simple theoretical method has been developed to study the thermal behaviour of nanomaterials by modifying the He and Yan (2001) model. This behaviour give vital information about their intrinsic structural characteristics. As external parameters like temperature, pressure, shape, size and dimensionality of nanomaterials change, their behaviour changes. He and Yan proposed an equation of state (assuming the Anderson–Grüneisen parameter (δ_T) to be independent of temperature) for the study of temperature effects on interatomic separation and bulk modulus of the bulk materials. In the present study, the He–Yan model has been modified by introducing the volume thermal expansion coefficient for nanomaterials (α_{0n}) in place of its bulk equivalent (α_0). The modified equation of state has been applied to four nanomaterials: silver (20 nm), aluminium (40 nm), nickel oxide (25 nm), and titanium dioxide (35 nm). The calculated results are compared with available experimental data and their bulk counterparts. It was found that the size-dependent properties of nanomaterials changes with the relative number of atoms present at the surface. Hence the energy linked with the atoms also changes. Consistency with experimental data supports the validity of the proposed model. Further, the effect of different shapes, viz. spherical nanomaterials (0D), nanowires (1D) and nanofilms (2D) on volume thermal expansion has also been studied: it varies with dimension due to the variation in surface-to-volume ratio.

Keywords: Anderson–Grüneisen parameter, equation of state, nanoparticles, nanotechnology, thermal properties

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1. Introduction

The considerably diverse properties of nanomaterials have attracted researchers for decades. At the nanoscale, the properties of elements depend on material size, shape and dimension (cf. changes in properties of semiconductors due to electronic confinement and of metals due to surface effects). Nanomaterials have been used in many fields, including medicine, biology, engineering, agriculture, physics and chemistry, due to the peculiar characteristics engendered by their significantly small size, and are having a great impact on both basic sciences and industrial applications. As object size decreases, thermal properties of the material also change; e.g., the surface energy of a crystal increases and in consequence the melting temperature decreases [1–3].

In the present work, we have developed an equation of state to study the thermal and dimension-dependent properties of nanomaterials by modifying the He and Yan equation [4]. Thermal studies of nanomaterials yield important information regarding interatomic separation and structure. Many effects have been observed, such as transformation of the nanoscale components and their interactions due to a change in temperature [5]. Among metal nanoparticles, those of silver and aluminium are prominent due to their wide range of applications. Aluminium nanoparticles can be produced at reasonable cost and are used in lubricants, solid rocket propellants and catalysts, etc. [6], whereas silver nanoparticles are antimicrobial and used in medicine and disinfection [7]. Among metal oxides, nickel oxide and titanium dioxide nanoparticles are used in many industrial applications [8–11].

2. Theoretical approach

The relationship between system variables like pressure, temperature and volume is known as the equation of state: it provides basic information about the system. An isobaric equation of state provides the relation between temperature and volume at constant pressure. He and Yan [1] have proposed a model to study the relative volumetric thermal expansion (V/V_0) of materials assuming that the Anderson–Grüneisen parameter (δ_T) is independent of temperature T:

$$V/V_0 = \exp[\alpha_0(T - T_0)\{1 + (1/2)\alpha_0\delta_T(T - T_0) + (1/3)\,\alpha_0^2\,\delta_T^2(T - T_0)^2\}] \tag{1}$$

where T_0 is a reference temperature. Eqn (1) can be modified for nanomaterials by incorporating the size and dimension effect on the bulk volume thermal expansion coefficient α_0 as suggested by Kumar et al. [12]. For spherical nanoobjects (i.e., nanoparticles) the volume thermal expansion is given as:

$$\alpha_{0n} = \alpha_0\,(1 - (2d/D))^{-1} \tag{2}$$

where d and D denote, respectively, the atomic diameter and particle size (i.e., diameter). The modified He–Yan equation for spherical nanoparticles can therefore be written as:

$$V/V_0 = \exp[\alpha_0\,(1 - (2d/D))^{-1}(T - T_0)\{1 + (1/2)\,\alpha_0(1 - (2d/D))^{-1}\delta_T(T - T_0) + (1/3)\,\alpha_0^2\,(1 - (2d/D))^{-2}\,\delta_T^2(T - T_0)^2\}] \tag{3}$$

For elongated nanoobjects (i.e., nanowires) of length L, we have

$$\alpha_{0n} = \alpha_0\,(1 - (4d/3L))^{-1}.$$

Thus for nanowires the modified He–Yan equation is:

$$V/V_0 = \exp[\alpha_0(1-(4d/3L))^{-1}(T-T_0)\{1+(1/2)\,\alpha_0(1-(4d/3L))^{-1}\,\delta_T(T-T_0)+ (1/3)\alpha_0^2(1-(4d/3L))^{-2}\,\delta_T^2(T-T_0)^2\}]. \quad (4)$$

For nanoobjects with only one dimension (i.e., height or thickness h) in the nanoscale (i.e., nanofilms or nanoplates), we have:

$$\alpha_{0n} = \alpha_0(1-(2d/3h))^{-1}$$

and the He–Yan equation becomes

$$V/V_0 = \exp[\alpha_0(1-(2d/3h))^{-1}(T-T_0)\{1+(1/2)\,\alpha_0(1-(2d/3h))^{-1}\,\delta_T(T-T_0)+ (1/3)\alpha_0^2(1-(2d/3h))^{-2}\,\delta_T^2(T-T_0)^2\}]. \quad (5)$$

Using eqns 3, 4 and 5, the relative volume thermal expansions of four kinds of nanoobjects, viz. silver (20 nm), aluminium (40 nm), nickel oxide (25 nm) and titanium dioxide (35 nm) particles, wires and films (i.e., having 0, 1 and 2 dimensions respectively in the nanoscale) have been studied. The Anderson–Grüneisen parameter δ_T is taken to have a value of 4 [13] and the other input parameters are given in Table 1.

Table 1. List of input parameters for the calculations.

Substance	D, L or h / nm	Coefficient of volume thermal expansion		d / nm
		α_0 / 10^{-5} K^{-1}	Ref.	
Ag	20	1.8	8	0.344
Al	40	7.8	14	0.286
NiO	25	3.9	11	0.704
TiO_2	35	1.5	9	0.734

3. Results and discussion

Relative volume thermal expansion (V/V_0) have been calculated for spherical nanoparticles using eqn (3) and compared with bulk data using eqn (1) (Fig. 1). The expansion of the nanomaterials is greater than that of their bulk counterparts at all temperatures. The explanation is that there are relatively more atoms present at the surface of nanoobjects compared with the bulk, as a result of which the surface energy of nanomaterials is higher and it expands more than the bulk. Further, using eqns (4) and (5) the volume thermal expansion for nanowires and nanofilms has been calculated likewise, and the results compared with each other and with those for the particles, along with available experimental data (Fig. 2). The volume thermal expansion is greatest for the spherical particles, followed by nanowires and nanofilms. It substantiates the fact that there are relatively more atoms present at the surface of spherical particles than at the surface of nanowires and nanofilms. Hence, less thermal energy is required to expand the spherical nanomaterial in comparison with a nanowire or nanofilm. The experimental data best matches the calculated results for the spherical nanomaterial, indicating that the most abundant shape of practically available nanomaterials is spherical.

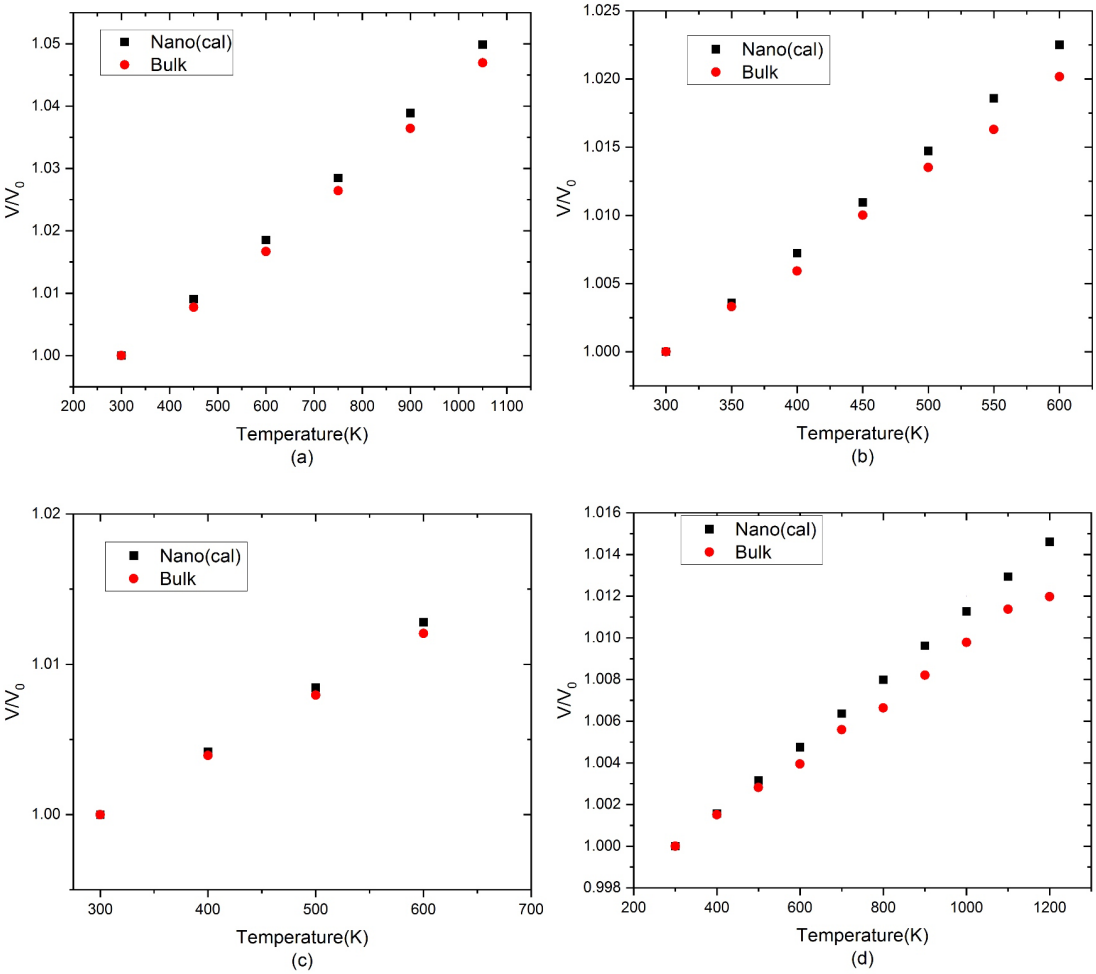

Figure 1. Temperature variation of volume thermal expansion V/V_0 for (a) silver (20 nm), (b) aluminium (40 nm), (c) nickel oxide (25 nm) and (d) titanium dioxide (35 nm) spherical nanomaterials compared with their bulk counterparts.

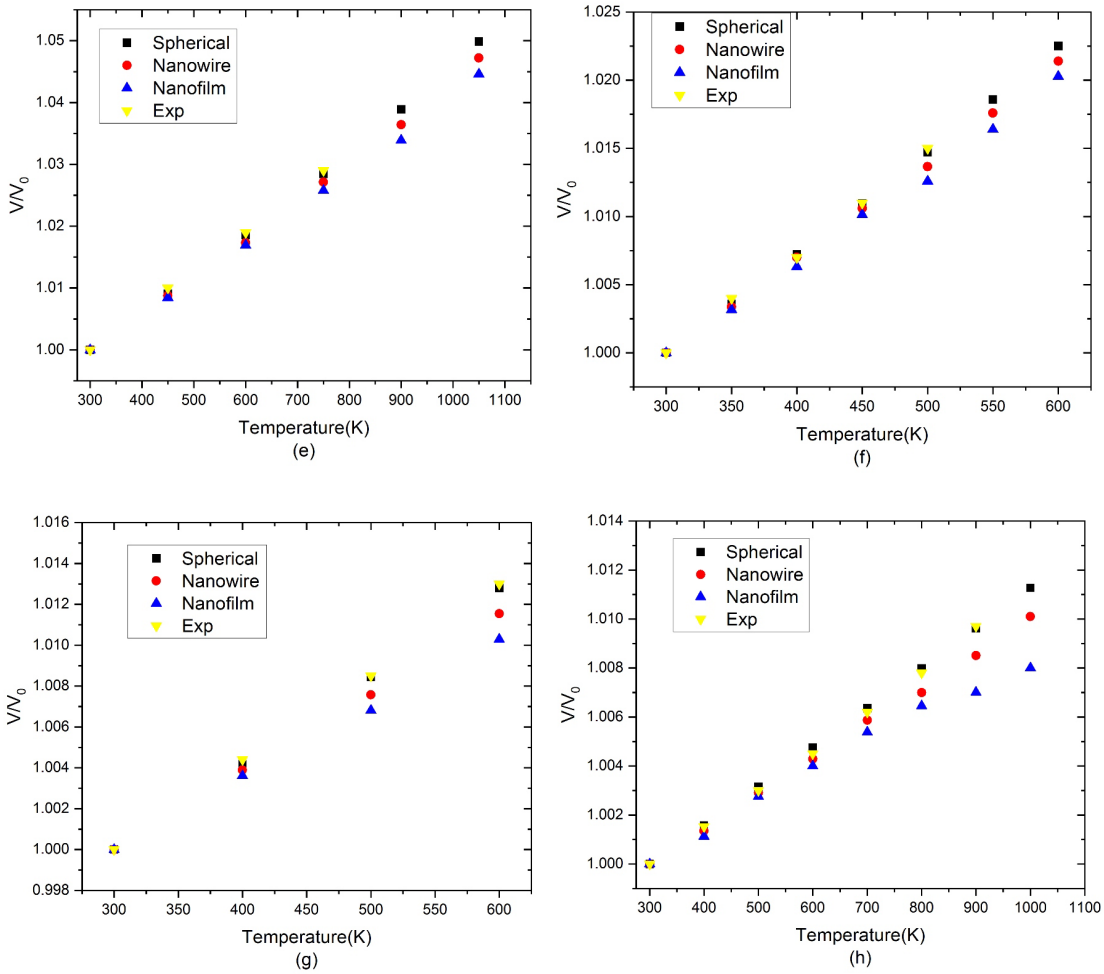

Figure 2. Volume thermal expansion V/V_0 for (e) silver (20 nm), (f) aluminium (40 nm), (g) nickel oxide (25 nm) and (h) titanium dioxide (35 nm) nanoobjects having different dimensionality (particles, 0D; wires, 1D; and films, 2D) and with experimental data (Ag [8], Al [14], NiO [11] and TiO_2 [9]).

4. Conclusions

Nanomaterials show greater volume thermal expansion in comparison to their bulk counterparts. The expansions of materials having different numbers of dimensions in the nanoscale, hence different surface-to-volume ratios, are commensurate with the relative numbers of surface atoms, which are bound with lower energy and hence easier to expand. Agreement with available experimental results supports the validity of the proposed equations.

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