

# Size dependent melting properties of Bi nanoparticles by molecular dynamics simulation

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Molecular Dynamics (MD) simulation has been used to investigate the size dependent melting properties of different shaped Bismuth nanoparticles. MD calculations for spherical and prism shaped nanoparticles are carried out using the interatomic interactions modelled by the Modified Analytic Embedded Atom Method (MAEAM) type many body potentials. The structural properties such as radial distribution functions and self diffusion coefficients of nanoparticles have computed at different temperatures. Size dependent melting temperature of different shaped nanoparticles with free surface has obtained from the thermodynamic model developed by Nanda. MD predictions and present theoretical results have been analyzed and compared with experimental data. Both particle size dependent melting temperature and shape effect have been determined. It has been shown that the melting temperature of prism shaped Bi nanoparticles depend on non-linearly on the particle size. In the present work, two different regimes are clearly noticed for different shape Bi nanoparticles.

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## 1. Introduction

In recent decades, researchers have paid more attention to nanomaterials because of their potential applications in areas such as magnetic data storage, electronics, catalysis etc. Nanomaterials can be classified into nanocrystalline and nanoparticles. It has been well established in experimentally [1-3] and theoretically [4-14] that the melting temperature of nanoparticles depends on the particle size which are different from that of the corresponding bulk materials. This attempt first confirmed experimentally has been made by Pawlow [1]. A lot of models try to explain the melting temperature depression of small particles [4-14]. It has been shown that thermodynamic model has lots of merits over other models and has been used by many researchers to understand the experimental results. Generally models for the prediction of nanoparticle melting temperature can be categorized into three groups [4] : i ) models based on classical thermodynamics and surface energy [1,4-6] ii ) models determined from molecular thermodynamics and mean square displacement (msd) [7-9], and iii ) models predicted from cohesive energy calculations of nanoparticles [10-14]. Thermodynamic models of nanoparticle melting are based on different processes which include the homogeneous melting hypothesis (HMH) [15, 16], liquid skin melting (LSM) [17], the liquid nucleation and growth (LNG) [18], liquid drop model (LDM) [10]. Now it is found that the melting temperature of nanoparticles is lower than the corresponding bulk materials as the phenomenon of melting point depression. Thermodynamic as well as other theoretical models assume spherical geometry for nanoparticles. However, it has been noted some researchers that free nanoparticles are not necessarily spherical [11, 15].

Recently, Nanda *et al* [14] have developed a model for prism shaped nanoparticles by using simple classical thermodynamic model including equilibrium between solid and melted particles. They have also studied the size dependent melting of prism-shaped indium nanoparticles by comparing the theoretical results with experimental data of Dippel *et al* [19].

A thermodynamic model for the melting temperature of nanoparticles with cylindrical geometry based on HMH and LNG process has been discussed by Nanda [15]. It can be applied to nanowires, nanorods and pancake-like nanoparticles.

All these recent theoretical and experimental studies [3, 11, 15] motivate us in order to study the size and shape dependent melting point depression of bismuth nanoparticles by molecular dynamics (MD) simulation method. According to our knowledge, no MD studies have so far been made for melting behaviours of bismuth nanoparticles with different shape. Therefore, it is needed to take the particle shape into consideration when developed models for the melting temperature of nanoparticles [11].

Bismuth has been chosen as a model system for the metallic nanoparticles. Main reason for this is while bismuth is semimetal at room temperature; it shows metallic properties in liquid state. Another significant property of Bismuth is, for the particles having radius length below 4 nm, reduction in the lattice parameter ratio may not change the crystal structure [20]. In recent work, the difference between theory and experimental results for the relationship between melting temperature and particle radius of those below 7nm has been reported by Allen *et al* [20].

In this contribution, the size and shape dependent melting temperature of Bi has been described for different number of spherical (dots) and prism shaped nanoparticles

in terms of thermodynamic model developed by Nanda *et al* [10, 14,15] and also by MD simulations.

The spherical nanoparticles with diameter around 3-9.0 nm and square prism shaped nanoparticles with the edge of D=3-10.0 nm and H= 8nm length have been studied in MD calculations. Both the theoretical and MD predictions for the melting temperature of different shape Bi nanoparticles have compared with each other and the available experimental values. As a result of that comparison two different regimes (I-II) are clearly noticed that is zero dimensional (0D) model for spherical shaped nanoparticles and one dimensional (1D) model for prism shaped nanoparticles. The quantitative dependence on  $T_m$  on particle diameter D that MD predictions for the melting temperature of prism shaped nanoparticles are in a good agreement with experimental data for the particles having diameter 7-10nm with 8nm height. In that region  $T_m$  depends nonlinearly on the inverse of the nanoparticle diameter, where there is a linear fit to the points derived for spherical nanoparticles by MD simulations. It is found that the particle shape have larger effect on small particles than on large particles. It is noticed that the zero dimensional model for spherical particles having diameter over 10nm may available.

This study may also provide for basis for gaining thermodynamics insights into size and shape control of metallic nanoparticles. The present theoretical and MD predictions of the particle shape effect on the melting temperature of metallic nanoparticles may be tested by further experiments

## 2. Model and method

### 2.1 Size-dependent melting temperature

The size-dependent melting temperature of  $T_m$  for the nanoparticles has been determined in terms of thermodynamic model based on different melting process [10, 14, 15]. In HMH, there is no surface melting because the entire melted particles are in equilibrium with entire solid ones.

The size dependent melting for the nanoparticles of spherical geometry with diameter D can be expressed as [10]

$$T_m = T_{mb} \left[ 1 - \frac{\beta}{D} \right] \quad (1)$$

where  $T_{mb}$  is melting temperature of corresponding bulk materials,  $\beta$  is a physical parameter obtained from the empirical relation given in [10].

The melting temperature for a particle with cylindrical geometry such as a nanowire and nanorod of length H and diameter D can be written as

$$T_m = T_{mb} \left[ 1 - \left( \frac{2}{D} + \frac{2}{H} \right) \beta \right] \quad \text{for HMH} \quad (2)$$

$$T_m = T_{mb} \left[ 1 - \left( \frac{4}{D} + \frac{2}{H} \right) \beta \right] \quad \text{for LNG} \quad (3)$$

The above equation can be applied for pancake-like nanoparticles [15]. On the other hand, the size-dependent melting of prism-shaped indium nanoparticles has been investigated by Dippel *et al* [19].

Recently, Nanda *et al* [14] have modified thermodynamic model assuming the equilibrium between solid and melted prism shaped nanoparticles [14, 15]. The melting temperature  $T_m$  of a prism shaped nanoparticle in the thermodynamic model is given by

$$T_m = T_{mb} \left[ 1 - \left( \frac{6.928}{D} + \frac{2}{H} \right) \beta \right] \quad (4)$$

where D is the edge length and H is the height of solid prism shaped nanoparticles,  $\beta$  is material dependent parameter as given in [10].

### 2.2 Interatomic pair potential

The interatomic interactions between Bi atoms are modelled by the Modified Analytic Embedded Atom Method (MAEAM) type many body potentials [21, 22]. In the MAEAM model, the total energy of a system  $E_{tot}$  can be written as

$$E_{tot} = \sum_i \sum_{j \neq i} \phi(r_{ij}) + \sum_i F(\rho_i) + \sum_i M(P_i) \quad (5)$$

$$\rho_i = \sum_{j \neq i} f(r_{ij}), \quad (6)$$

$$P_i = \sum_{j \neq i} f^2(r_{ij}), \quad (7)$$

where  $r_{ij}$ , is the separation distance of atom  $j$  from atom  $i$ ,  $\phi(r_{ij})$  is the pair potential as a function of the distance  $r_{ij}$ ,  $F(\rho_i)$  is the energy to embed an atom in site  $i$  with electron density  $\rho_i$  which is given by a linear superposition of spherical averaged atomic electron density of other atoms,  $f(r_{ij})$ .  $M(P_i)$  is the modified term, which describes the energy change due to nonspherical distribution of atomic electronic density and deviation from the linear superposition. Pair potential  $\phi(r_{ij})$  can be given as the following forms, other MAEAM functions as in [21, 22]

$$\phi(r_{ij}) = k_0 + k_1 \left( \frac{r_{ij}}{r_{1e}} \right)^2 + k_2 \left( \frac{r_{ij}}{r_{1e}} \right)^4 + k_3 \left( \frac{r_{1e}}{r_{ij}} \right)^4, \quad (8)$$

$$F(\rho_i) = -F_0 \left[ 1 - n \ln \left( \frac{\rho_i}{\rho_e} \right) \right] \left( \frac{\rho_i}{\rho_e} \right)^n, \quad (9)$$

$$M(P_i) = \alpha \left\{ 1 - \exp \left[ -10000.0 \left( \ln \left( \frac{P_i}{P_e} \right) \right)^2 \right] \right\}, \quad (10)$$

$$f_e(r_{ij}) = f_e \left( \frac{r_{1e}}{r_{ij}} \right)^6, \quad (11)$$

where subscript  $e$  indicates equilibrium and  $r_{1e}$  is the first-neighbour distance in the equilibrium state. The electron density at equilibrium state  $f_e$  is chosen as [23]

$$f_e = \left( \frac{E_c - E_{1v}^f}{\Omega} \right)^{3/5} \quad (12)$$

where  $\Omega$  denotes the atomic volume. The model parameters  $k_0, k_1, k_2, k_3, F_0, n$  and  $\alpha$  are determined by fitting the physical properties of Bi, such as cohesive energy  $E_c$ , vacancy formation energy  $E_{1v}^f$ , lattice parameter  $a_0$  and elastic constants  $C_{11}, C_{12}$  and  $C_{44}$ .

### 2.3 Molecular dynamics simulation procedure

The initial configurations of spherical five nanoparticles, with the number of atoms from ranging 640 to 17297atom (nanoparticle diameter around 3-9.0 nm) are extracted from a large the bcc crystal structure of Bi block, using a series of spherical cut-off centred at a core of

cubes. The square prism shaped six nanoparticles with the number of atoms from ranging 2688 to 26250 are extracted the edge length of prism  $D=3-10.0$  nm with height  $H=8$ nm.

All of the atoms are located on their lattice positions. The stable structure at 0 K is obtained through the initial configurations annealed fully at  $T=100$  K and then cooled to  $T=0$  K at a cooling rate 1 K/ps. In order to get an energy-optimized structure during heating at a given temperature for the bulk systems it is performed molecular dynamics under constant temperature and constant pressure condition (NPT) with a periodic boundary conditions. For the nanoparticles, we used the constant volume and constant temperature (NVT) molecular dynamics without the periodic boundary conditions. The temperature is controlled by Nose-Hoover thermostat. The Newtonian equations of motion are integrated using the Leapfrog Verlet method with a time step of 1 fs. For each nanoparticle, the system is relaxed 50000 time steps (50 ps) at various temperatures far from the melting region, while at several points near the melting point ( $T_m$ ) the systems are relaxed for 100000 time steps (100 ps).

### 3. Results and discussion

In this work the model parameters of Bi potential are determined by fitting the physical properties and elastic constants which are taken from [24]. In the present MAEAM model, the two-body potential and the electron density functions are cut off using the procedure proposed by Zhang *et al* [22] with the start point  $r_s=r_2$  and the end point  $r_c = 0.86a_0$ , where  $r_2$  is the second-neighbor distance.

The input physical parameters are listed in Table 1, and the calculated MAEAM model parameters for Bi are given in Table 2.

Table 1. Input parameters.

Metal	$E_c$ (eV)	$E_{1v}^f$ (eV)	$a_0$ (Å)	$C_{11}$ (eV/Å <sup>3</sup> )	$C_{12}$ (eV/Å <sup>3</sup> )	$C_{44}$ (eV/Å <sup>3</sup> )
Bi	1.75	0.5	3.88	0.390	0.132	0.064

Table 2. The MAEAM model parameters for Bi

Metal	$F_0$ (eV)	$n$	$\alpha$ (eV)	$f_e$ (eV/Å <sup>3</sup> )	$k_0$ (eV)	$k_1$ (eV)	$k_2$ (eV)	$k_3$ (eV)
Bi	1.25	0.361	0.127	0.150	-0.231	0.072	0.035	0.045

In the present work, melting evolution has been investigated in two different shape Bi nanoparticles. The spherical five different Bi nanoparticles has been studied with the number of atoms from ranging 640, 2162, 5125, 10010 and 17297 atoms (nanoparticle diameter around 3-9.0 nm). Melting process of square prism shaped six Bi

nanoparticles has been studied with the number of atoms from ranging 2688 to 26250 (edge of prism  $D=3-10.0$  nm with  $H=8$ nm). Samples for prism shaped nanoparticle used in MD simulations are shown in Fig 1.

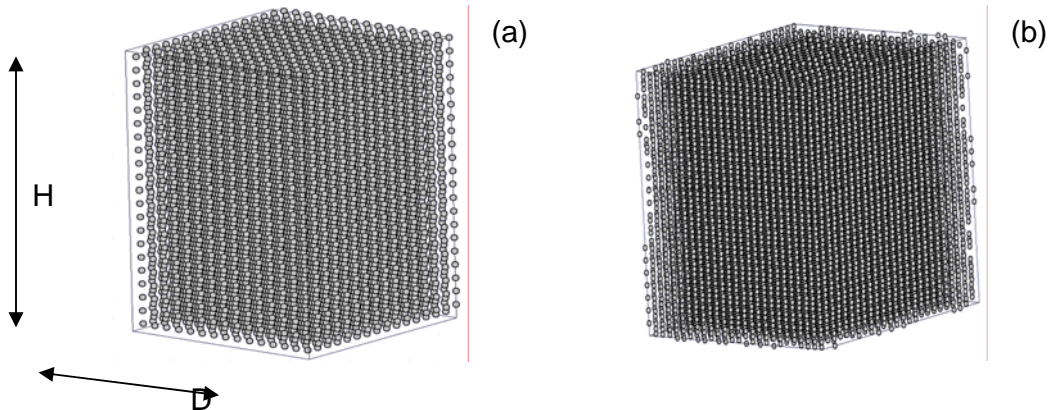


Fig. 1. MD samples for prism shaped nanoparticle at 0K a)  $D=6\text{nm}$  with  $H=8\text{nm}$  b)  $D=10\text{ nm}$  with  $H= 8\text{ nm}$

The equilibrium of the different shaped nanoparticles during heating are shown in Figure 2. The equilibrium shapes for spherical nanoparticles  $N=10010$  ( $D\approx 7,5\text{nm}$ ) at

470K, just below melting, have obtained that the nanoparticle is almost spherical. Above melting, the spherical nanoparticle is essentially a perfect sphere.

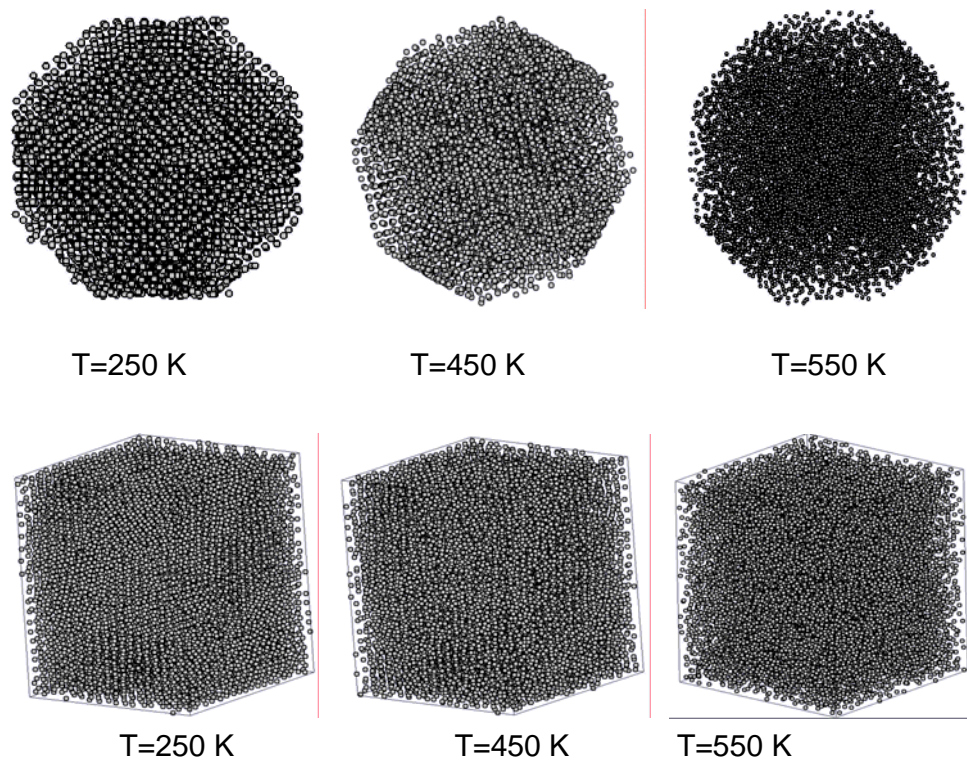


Fig. 2. Section snapshot views of the MD sample for Bi nanoparticles at a series of temperatures during heating with (a)  $N = 10010$  atoms for spherical ( $D\approx 7.5\text{ nm}$ ) (first row) (b)  $N=13608$  atoms for prism shaped ( $D=7\text{nm}, H=8\text{nm}$ ) (second row).

In MD simulations, the melting point of bulk Bi is as 500K, it is close to the experimental value of  $T_m = 544\text{K}$  [24]. The size dependence of the different shaped nanoparticles obtained by thermodynamic models is shown in Figure 3 along with experimental data and MD predictions as a function of the inverse size of nanoparticle diameter. The melting temperature of spherical, pancake like and prism shaped bismuth nanoparticles has

determined from Eqs. 1, 3, 4 respectively. In Figure 3, the values for spherical nanoparticles are taken from Ref. [10] which was obtained by liquid drop model. For prism shaped nanoparticles, we used  $\beta=0.13081\text{ nm}$  and

$$\beta = \frac{\gamma_{sl}}{\rho_s L_b}, \quad \text{where} \quad \gamma_{sl} = 69 \times 10^{-3} \text{ J/m}^2,$$

$\rho_s = 9.75 \times 10^3 \text{ kg/m}^3$ ,  $L_b = 54.1 \times 10^3 \text{ J/kg}$  [25].

For pancake-like nanoparticles, the value of  $\beta=0.86\text{nm}$  is used. In figure 3, the plotted melting temperature of prism-shaped and pancake-like bismuth nanoparticles are shown for different edge length (as corresponds nanoparticle diameter) but 8nm height ones. The experimental data drawn in Figure 3 is taken from Ref. [11, 20] and analysed together with both theoretical and MD predictions. Two different regimes (I-II) are clearly noticed in Fig.3. It may be noted that the extrapolated bulk melting temperature is closer to the experimental one for large H value of prism shaped Bi nanoparticles.

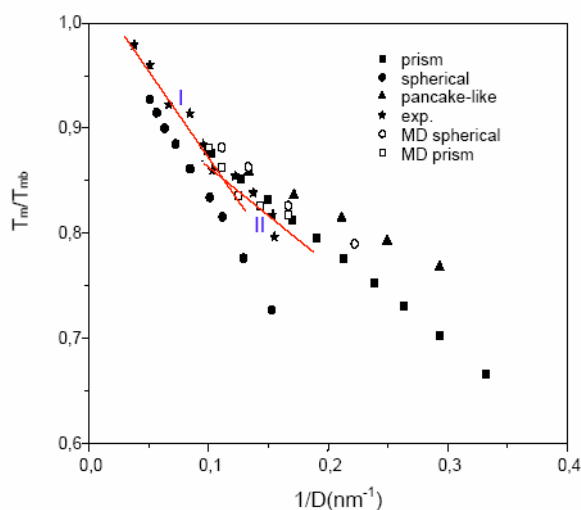


Fig. 3. Two different regimes in size dependent melting for Bi nanoparticles vs. the reciprocal of nanoparticle Diameter.

The obtained MD results are compared with others separately for both regimes in Figure 4. This indicates that one dimensional (1D) model is more applicable to region II than zero dimensional one. The melting point deduced from thermodynamic model for (6-10nm edge length with 8nm height) prism shaped nanoparticles decreases linearly with the reciprocal of the nanoparticle size in region II. This result is in a good agreement with experimental data replaced in this region. However, MD predictions for prism shaped nanoparticles are closer to all experimental data than other theoretical predictions and MD results for spherical shaped nanoparticles. As a result of MD predictions corresponding to the same sample of prism shaped nanoparticles, there is a non-linear relationship between the melting temperature and inverse of the particle size in 1D model.

In other words, the presented model is better than the liquid drop model in predicting the melting temperature of non-spherical nanoparticles. For spherical nanoparticles, the experimental results are close to our theoretical results in zero dimension model when the particle diameter D is larger than about 10nm, It has been suggested by Qi and

Wang [11] that the shape of nanoparticles may be in spherical when the particle size is large, and in polyhedral shape when the particle size is small. It has been confirmed by MD simulations and thermodynamic models.

It has found that the particle shape has larger effect on small particles than on large particles.

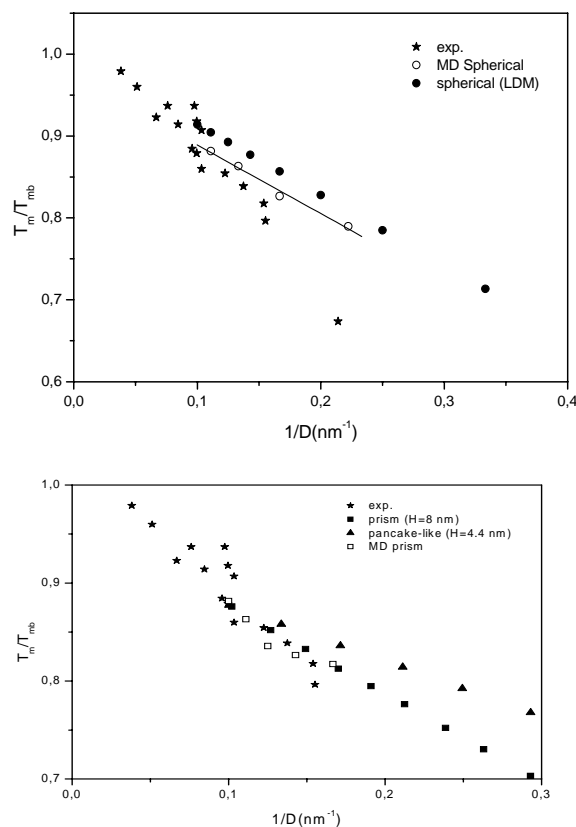


Fig. 4. Size dependence vs. the reciprocal of nanoparticle diameter for (a) spherical shaped nanoparticles as zero dimensional (0D) model (b) prism shaped nanoparticles as one dimensional (1D) model.

Fig. 5 shows Arrhenius's plots for the average diffusion coefficient of different shaped nanoparticles. However there is average fit in Figs 5, it reveals that the diffusion behaviour of nanoparticles is dominated by the surface atoms and also shows 2 stages for diffusion process. The first stage corresponds to the diffusion process below the melting point, and the other represents the diffusion process above the melting point.

The temperature dependence of the diffusion coefficient for two different shaped nanoparticles is shown in Figure 6. As discussed above, the two stages for diffusion process may be noted clearly in Figure 6. As shown in Figure 6, when the temperature approaches melting point, a sudden increase in the diffusion coefficient can be observed for all nanoparticles. Furthermore, even above the melting temperature, the larger nanoparticles have lower diffusion coefficients than smaller nanoparticles.

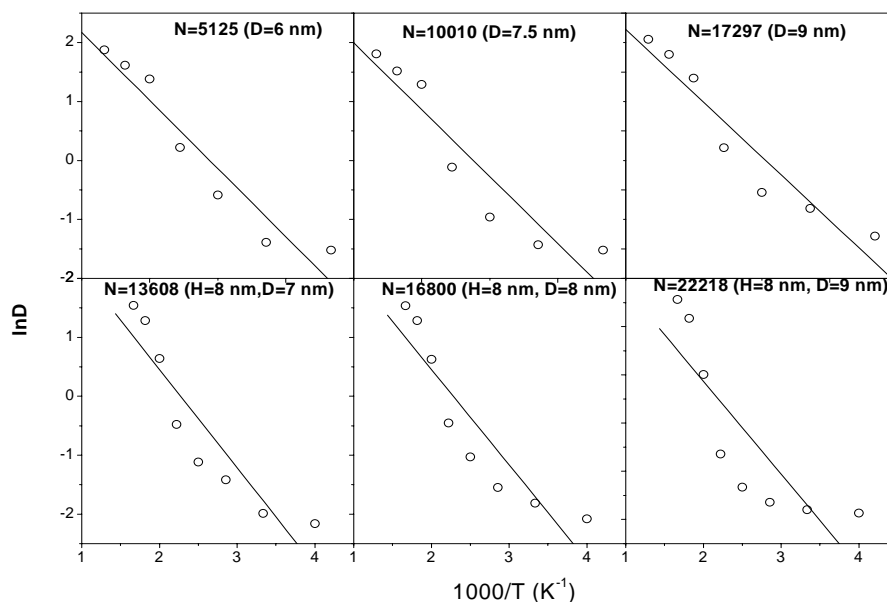


Fig. 5. Arrhenius's plot for the average diffusion coefficient of a) spherical nanoparticles with various diameters (first row) b) prism-shaped nanoparticles (second row).

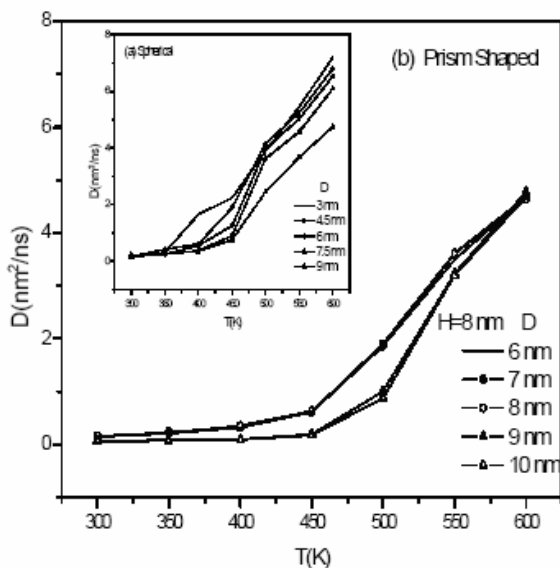


Fig. 6. Temperature dependence of the diffusion coefficient for different shaped nanoparticles

Consistent with the above discussions, it is related with the surface to volume ratio because the atoms on the surface layers have a very high diffusion coefficient. Both different shaped samples exhibit similar diffusion behaviour for particle diameter of those below 7 nm.

With the reduction of nanoparticle size, the fraction of surface atoms increases and the melting point decreases. On the other hand, it is observed that the heat of melting for the nanoparticles is much lower than that of the bulk Bi and also decreases linearly with the reciprocal of the nanoparticle size. The obtained heat of fusion of bulk Bi is about  $0.013\text{ eV}$ , which is much lower to the experimental value of  $\Delta H_m = 11.3\text{ kJ/mol} = 0.103\text{ eV/atoms}$  [25, 26].

In the experimental studies, it is observed that the melting phenomena on a particle is just the surface liquid skin resulted by surface premelting. However, the melting process and melting mechanism of nanoparticles can be analysed in details using molecular dynamics simulation. The structures of the simulated spherical and square prism shaped Bi particles are discussed in terms of the radial distribution functions as a function of number of the particles in Fig. 7



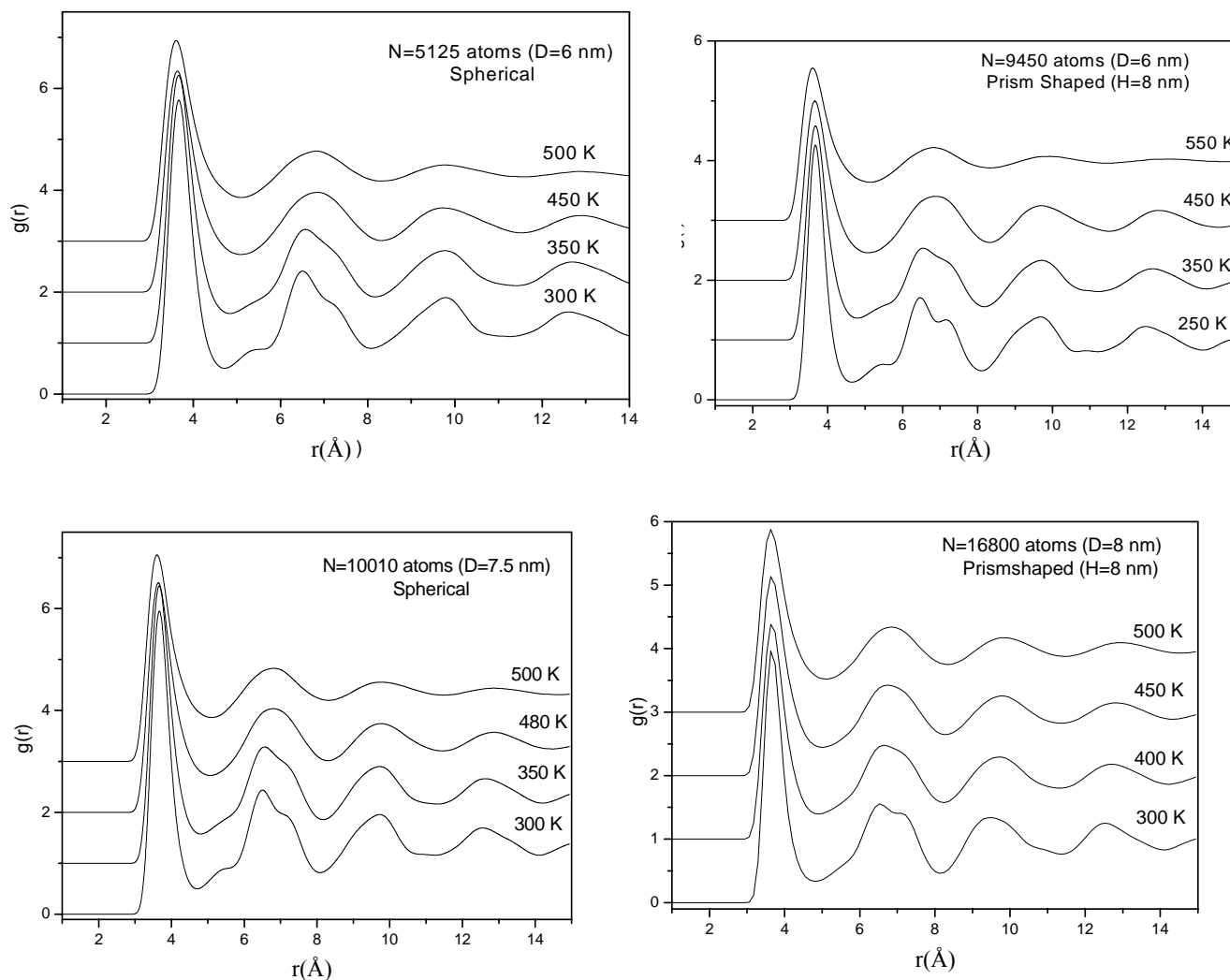


Fig. 7. The radial distribution functions (RDF) for spherical and prism shaped Bi nanoparticles with different number of atoms at a series of temperatures during heating

There exists obvious short-range order in the Bi nanoparticles at high temperature which is typical structural feature of liquid metals. At low temperatures, first peak becomes increasingly sharp. In present study, the RDF analysis shows that there is no structural transformation prior to melting in bcc bismuth.

#### 4. Conclusions

In this paper, it has been investigated the melting evolution of Bi nanoparticles of a few thousand atoms which form spherical and prism shaped with molecular dynamics simulation using the modified analytic embedded atom method. It has been also shown that thermodynamic model can be applied to understand the

size dependent melting temperature of any shape nanoparticles provided the expression for the melting temperature based on the shape of the nanoparticles. However, MD predictions for prism shaped nanoparticles are closer to all experimental data in the region for the particle having diameter (edge length) 6-10nm. As a result of MD predictions corresponding to the same sample of prism shaped nanoparticles, there is a non-linear relationship between the melting temperature and inverse of the particle size in that region. It has observed that the bulk melting temperature cannot be extrapolated from both experimental and presented nanoscale results. The size dependent heat of fusion can not explain the observed size dependent melting behaviour of Bi prism shaped nanoparticles.

As a result, two different regimes (I-II) are clearly noticed that is zero dimensional (0D) model for spherical shaped nanoparticles and one dimensional (1D) model for prism shaped nanoparticles. Indeed, this phenomenological model presented in this work predicts a crossover between (1D) and (0D) dimensional systems. These results open a new approach to investigate the size dependence melting of different shaped metallic nanoparticles.

## References

- [1] P. Pawlow, *Z. Phys. Chem.* **74**, 562 (1910).
- [2] F. Wang, R. Tang, H. Yu, P. C. Gibbons, W. E. Buhro, *Chem. Mater.*, **20**(11), 3656 (2008).
- [3] M. S. Dresselhaus, Y.-M. Lin; O. Rabib, A. Jorio, A. G. Souza Filho, M. A. Pimenta; R. Saito, G. G. Samsonidze, G. Dresselhaus, *Mater. Sci. Eng., C* **23**, 129 (2003).
- [4] M. Mirjalili, J. Vahdati-Khaki, *J. Phys. Chem. Solids*, **69**, 2116 (2008).
- [5] Ph. Buffat, J.P. Borel, *Phys. Rev.* **A13**, 2287 (1976).
- [6] J. Sun, S. L. Simon, *Thermochim. Acta* **463**, 32 (2007).
- [7] Q. Jiang, Z. Zhang, J. C. Li, *Acta Mater.* **48**, 4791 (2000).
- [8] L. H. Liang, J. C. Li, Q. Jiang, *Physica* **B334**, 49 (2003).
- [9] W. Hu, S. Xiao, J. Yang, Z. Zhang, *Eur. Phys. J. B* **45**, 547 (2005).
- [10] K. K. Nanda, S. N. Sahu, S. N. Behera, *Phys. Rev.* **A66**, 013208 (2002)
- [11] W. H. Qi, M. P. Wang, *Mater. Chem. Phys.* **88**, 280 (2004).
- [12] W. H. Qi, M. P. Wang, M. Zhou, X. Q. Shen, X. F. Zhang, *J. Phys. Chem. Sol.* **67**, 851 (2006)
- [13] M. Attarian Shandiz, A. Safaei, S. Sanjabi, Z. H. Barber, *Solid State Commun.* **145**, 432 (2008).
- [14] D. Sar, P. Nayak, K. K. Nanda, *Phys. Lett.* **A372**, 4627 (2008)
- [15] K. K. Nanda, *Pramana- J. Phys.*, **72**, 617 (2009).
- [16] J.-P. Borel, *Surf. Sci.* **106**, 1 (1981).
- [17] K. J. Hanszen, *Z. Phys.* **157**, 523 (1960).
- [18] S. C. Hendy, *Nanotechnol.* **18**, 175703 (2007).
- [19] M. Dippel, A. Maier, V. Gimple, H. Wider, W. E. Evenson, R. L. Rasera, G. Schatz, *Phys. Rev. Lett.* **87**, 095505 (2001).
- [20] E. A. Olson, M. Yu. Efremov, M. Zhang, Z. Zhang, L. H. Allen, *J. Appl. Phys.*, **97**, 034304 (2005).
- [21] S. Senturk Dalgic, see the special issue NATO-OTAN Book Series B-C: Nanostructured Materials for Advanced Technological Applications, p.87, (2009).
- [22] J. M. Zhang, G. X. Chen, K. W. Xu, *Physica B* **390**, 320 (2007).
- [23] W. Y. Hu, B. W. Zhang, X. L. Shu, B. Y. Huang, *J. Alloys Compounds* **289**, 159 (1999).
- [24] A. Landa, P. Wynblatt, A. Girshick, V. Vitek, A. Ruban, H. Skriver, *Acta Mater.* **46**, 3027 (1998).
- [25] Q. Jiang, H. M. Lu, *Surface Science Reports* **63**, 427 (2008).
- [26] C. Kittel. *Introduction to the physics of the solid state*, 3<sup>rd</sup> edition (1981).

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