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Search of a model for melting temperature and cohesive energy of nanomaterials

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Three different models *viz.* Nanda model, Jiang model and BK model with different physical origin have been used to study the size dependence of melting temperature and cohesive energy of nanomaterials. A critical analysis demonstrates that the suitability of Jiang model or Nanda model depends on the material considered. Moreover, BK model works well for different nanomaterials considered in the present work. This demonstrates the suitability of the models proposed earlier. We therefore, extend the BK model for the size dependence of cohesive energy and Debye temperature. Nanda model has been found to give the reverse trends for the size dependence of cohesive energy as observed experimentally. However, Jiang model and BK model give similar trends of variation as observed experimentally. A comparison of the computed results with the experimental data demonstrates the superiority of the BK model. We also extend the BK model for the study of size dependence of Debye temperature. A good agreement between theory and experiment demonstrates the validity of the model proposed.

Keywords: Melting temperature, Cohesive energy, Debye temperature, Nanomaterials

1 Introduction

Nanoparticles have attracted increasing attention in the material science[1,2]. Melting is a very common phenomenon but not well defined for nanomaterials. Different theories of melting have been proposed[3], which are still waiting for their extension for nanomaterials. It has been observed that the melting temperature of metallic, organic and semiconductor nanoparticles decreases with the decrease of their particle size[4-7]. Melting point depression and enhancement of nanocrystals have been found to depend on size, dimension and surface conditions of nanocrystals[8]. A phenomenological model without adjustable parameters for size and dimension dependence of melting point depression and enhancement of nanomaterials has been introduced[9]. The predictions of the model have been found to be consistent with the experimental data and other thermodynamic models for metallic nanocrystals. The differences with other theoretical considerations have been discussed. The model has been extended for the size dependence of cohesive energy[9]. Nanda *et al.*[10] derived an expression for the size dependent melting of low dimensional systems on the basis of an analogy with the liquid drop model and empirical relations of bulk solids. A comparison with the other theoretical models as well as available experimental data has been presented. The model has been used to understand the effect of substrate temperature on the size of the deposited cluster and superheating of nanoparticles embedded in a matrix. An empirical relation for the size dependence of cohesive energy has also been proposed.

A simple model has been developed to understand the size and shape dependence of melting and superheating of nanomaterials[11]. The size dependence of melting temperature of free standing nanoparticles as well as embedded nanoparticles has been reported. The formulation has been used to study the effect of shape on melting temperature during the reduction of size. The results have been compared with the available experimental data. A good agreement between model predictions and experimental data has been observed. In the present paper, we extend the model to study the size dependent of cohesive energy and Debye temperature. Thus, there are different models based on different physical origins for the size dependence of melting temperature and cohesive energy. It is therefore, legitimate and may be useful to present a comparative study of all these models in the light of experimental data. This may help the researchers to use a more suitable model for further studies of size dependent properties of nanomaterials.

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2 Different Models of Melting and Cohesive Energy

According to Jiang model[8,12-15], the size dependent melting of free and embedded nanoparticles can be written as:

$$\frac{T_{mn}}{T_{mb}} = \frac{\sigma_b^2}{\sigma_n^2} = \exp\left[\frac{(1-\alpha)}{D/D_0 - 1}\right] \quad \ldots (1)$$

Eq. (1) is referred as Jiang model, T_{mn} is the melting temperature of the nanomaterial with diameter D, σ_n^2 is the average mean square displacement (MSD) of atoms and T_{mb} and σ_b^2 are their corresponding bulk values, α is the ratio between MSD of atoms at the surface and that within the material. D_0 denotes the critical diameter at which all the atoms of a nanomaterials are located on the surface which is given as:

$$D_0 = 2(3-d')\,d \quad \ldots (2)$$

where d is the atomic diameter and d' is a dimension dependent parameter. $d' \leftarrow 0$ for nanoparticles, $d' \leftarrow 1$ for nanowire and $d' \leftarrow 2$ for thin films as discussed in detail by Jiang *et al.*[8,9] Based on Mott's criterion for vibrational melting entropy at melting temperature of bulk material, following relation has been reported to calculate α for nanomaterials with free surfaces or that deposited on inert substrate[8,9].

$$\alpha = \left(\frac{2S_{vib}}{3R} + 1\right) \quad \ldots (3)$$

Here R is the universal gas constant. For metals, S_{vib} is approximately equal to the melting entropy (S_m) which is related to the melting enthalpy (H_{mb}) of bulk material by following relation:

$$S_{vib} = S_m = \frac{H_{mb}}{T_{mb}} \quad \ldots (4)$$

and cohesive energy is described by the following relation[9]:

$$\frac{E_n}{E_b} = \exp\left[\frac{(1-\alpha)}{\left(D/D_0 - 1\right)}\right] \times \left[1 - \frac{1}{\left(D/D_0 - 1\right)}\right] \quad \ldots (5)$$

where E_n and E_b are the cohesive energy of nano and bulk material, respectively. In Eq. (5), $D_0 = h/2$ and h denotes the atomic or molecular diameter as discussed earlier[9]. Jiang model was found successful to study the size and dimension dependent melting and superheating for nanomaterials.

The liquid drop model has been used by Nanda *et al.*[10] to derive an expression for size dependent melting of nanomaterials. According to this model, melting of spherical nanoparticles can be written as:

$$T_{mn} = T_{mb}\left(1 - \frac{\beta}{D}\right) \quad \ldots (6)$$

where β is a constant depending on the material and can be calculated by the known values of atomic volume (V_0), T_{mb} and coefficient of surface energy (γ) of the material with the help of following relation[10]:

$$\beta = \frac{6V_0\gamma}{0.0005736\,T_{mb}} \quad \ldots (7)$$

and the relation for cohesive energy reads as follows:

$$a_{v,d} = a_v - \frac{6V_0\gamma}{D} \quad \ldots (8)$$

where a_v is the cohesive energy of bulk material, V_0 is the atomic volume and γ is the coefficient of surface energy.

Qi[16] developed a simple model and predicted that the melting temperature of free standing nanosolids decreases with decrease in the particle size. The results have been reported for Sn and Pb nanoparticles and In (nanowire and nanofilm). A good agreement between theoretical and experimental results demonstrates the validity of the model proposed. A detailed discussion of this model has been provided by Bhatt and Kumar[11] by generalizing the model for different cases. The detailed analysis is available elsewhere[11] and the mathematical form reads as follows:

$$T_{mn} = T_{mb}\left(1 - \frac{N}{2n}\right)^k \quad \ldots (9)$$

where N is the number of surface atoms and n is the total number of atoms in nanosolid and k is a dimensionless parameter, which may have different

values. It has been discussed that the positive value of k gives the effect of size on the melting temperature of free standing nanosolids. The negative value gives the size effect on superheating of nanoparticles embedded in other host materials. If $k\rightarrow 0$ the size effect is very low. Further if $k=0$ the material can be treated as bulk material with no size effect, as summarized by Bhatt and Kumar[11]. It should be mentioned here that for $k=1$, Eq. (9) reduces to the relation of size dependence of melting temperature as proposed by Qi[16].

Now, following the arguments of Qi[16], we can write the relation of cohesive energy using Eq. (9) which reads as follows:

$$E_n = E_b\left(1-\frac{N}{2n}\right)^k \quad \ldots (10)$$

In Eq. (10), $N/2n$ depends on the shape and size of nanomaterial and can be calculated easily using simple geometry[11]. For spherical shape $N/2n = 2d/D$, where d is the diameter of atom and D is the diameter of nanosolid. The theory may be extended to study the size dependence of Debye temperature of nanomaterials. Using Lindemann criterion of melting, Das[17] has reported the following relation:

$$\theta_D = const\left(\frac{T_m}{MV^{2/3}}\right)^{1/2} \quad \ldots (11)$$

where θ_D is the Debye temperature, M is the molecular mass and V is the volume per atom. Using Eq. (11), Liang and Baowen[18] reported the following relation:

$$\left(\frac{\theta_{Dn}}{\theta_{Db}}\right) = \left(\frac{T_{mn}}{T_{mb}}\right)^{1/2} \quad \ldots (12)$$

where θ_{Dn} is the Debye temperature of nanomaterial and θ_{Db} the Debye temperature of corresponding bulk material. Combining Eqs (9) and (12), we get the following relation:

$$\theta_{Dn} = \theta_{Db}\left(1-\frac{N}{2n}\right)^{k/2} \quad \ldots (13)$$

Thus, there are different relations in different models for the size dependence of melting temperature, cohesive energy and Debye temperature. It is therefore, legitimate and may be useful to discuss these formulations in the light of experimental data and judge on the suitability of one over other.

3 Results and Discussion

It is very clear from above discussion that there are mainly three different models based on different physical origins. These models provide the size dependence of melting temperature and cohesive energy of nanoparticles. To make a more critical test, we used all these models to study the size dependence of melting temperature and cohesive energy of different nanoparticles for which experimental data are available. The input parameters[10,19] required for the present work are given in Table 1. The results obtained for size dependence of melting temperature of Ag nanoparticle are reported in Fig. 1 along with the available experimental data[20]. It is found that Nanda model Eq. (6) as well as BK model Eq. (9) gives similar results, which are in good agreement with the experimental data. However, Jiang model Eq. (1) is found to deviate as far as experimental results are concerned. In the case of Al nanoparticle, all the models give the similar trend of variation as shown in Fig. 2. The experimental data[21] lies in between the results obtained from BK model and Nanda model. The deviations are noted in Jiang model. The results

Table 1 – Input parameters[10,19] used in the present work.

Material	d (nm)	β (nm)	V_0 (cm^3/mol)	γ (mJ/m^2)	H_{mb} (kJ/mol)	T_{mb} (K)	E_b (kJ/mol)
Ag	0.304	0.96564			11.3	1235	
Al	0.252	1.2	10	1032	10.789	933.5	-327
Au	0.2884	1.1281			12.5	1337.58	
Bi	0.348	2.1273				544.6	
In	0.324	2.65			3.281	429.8	
Pb	0.35	1.7957			4.77	600.7	
Sn	0.28	2.2784			14.346	505.1	
W	0.31				35	3695	-824
Mo	0.31				36	2896	-598

obtained for Au nanoparticle are reported in Fig. 3. It is found that the result obtained from Nanda model and BK model are very close to each other. These results agree well with the experimental data when the particle size is very small. Both these models give slightly lower values as compared with the experimental data[22] by increasing size. The Jiang model is found to deviate though the trend of variation is similar. The results obtained for Bi are reported in Fig. 4. It is found that BK model gives better results as compared with the Nanda model and Jiang model deviate as compared with the experimental data[23]. It seems that the performance of Nanda model or Jiang model depend on the material considered. We have repeated our computational work for In (film). The results obtained are reported in Fig. 5. Jiang model and BK model give similar results which are in good agreement with the available experimental data[24]. The Nanda model is found to deviate largely. Similarly, situation arises for In (spherical and wire) as reported in Fig. 6 and Fig. 7 in the light of experimental data[25, 26].

The results obtained for Pb (spherical) are reported in Fig. 8. All the models are found to give similar trends of variations. The experimental data[27] are found to be slightly higher and are close to the BK model. In this case, the theory does not agree well with experimental results as in the other nanosolids. Therefore, it may be recommended to look once again on the experimental data[27]. The results obtained for

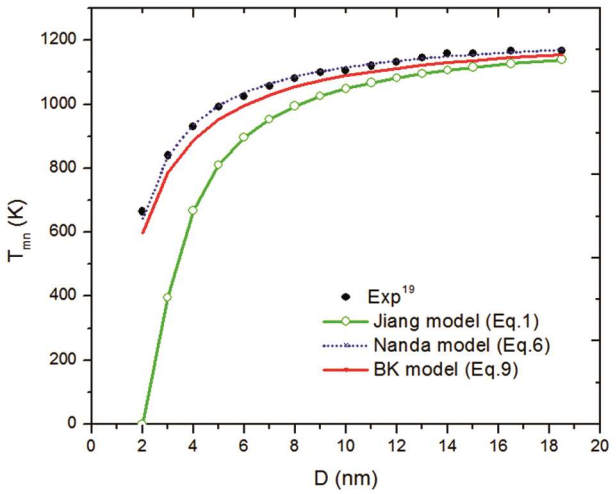

Fig. 1 – Size dependence of melting temperature for Ag (spherical).

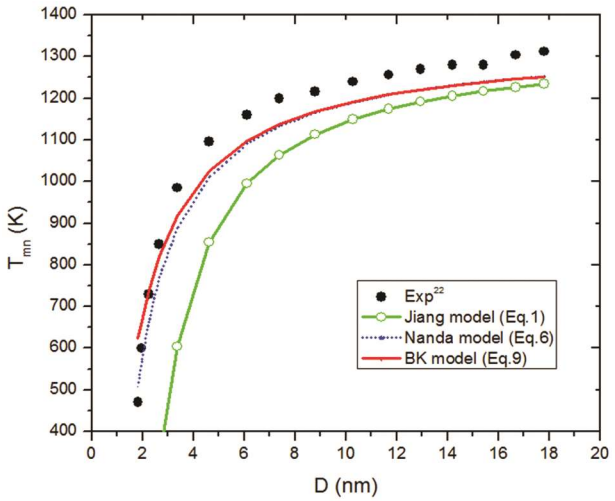

Fig. 3 – Size dependence of melting temperature for Au (spherical).

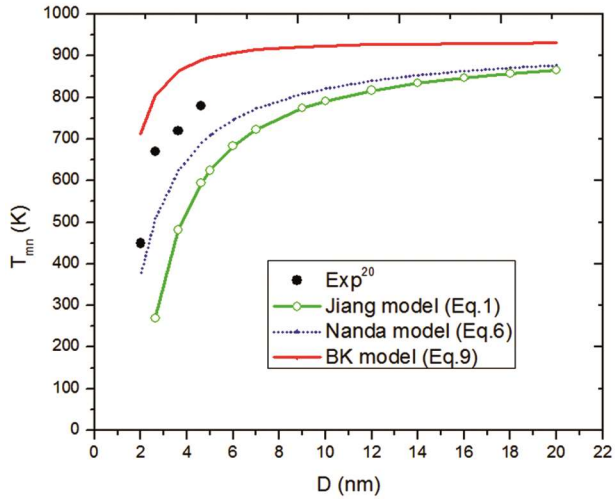

Fig. 2 – Size dependence of melting temperature for Al (spherical).

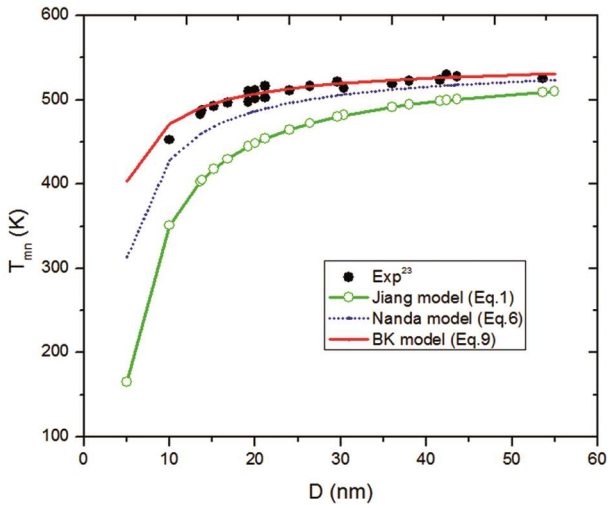

Fig. 4 – Size dependence of melting temperature for Bi (spherical).

Sn (spherical) are reported in Fig. 9. The trends of variation are similar in theory and experiment[28,29]. The results obtained by BK model are close to experimental data and Nanda model deviate largely. To conclude, the performance of the models is summarized in Table 2. It seems that the performance of Jiang model as well as Nanda model depends on material considered. Their deviations are noted by changing the material. However, BK model has been found to be good for all the materials considered in the present paper. This demonstrates the superiority of BK model as compared with Jiang model and Nanda model for the size dependence of melting temperature of nanomaterials.

For a more critical test of the theory, we extend these models to study the size dependence of cohesive energy. Actually, nanomaterials have attracted

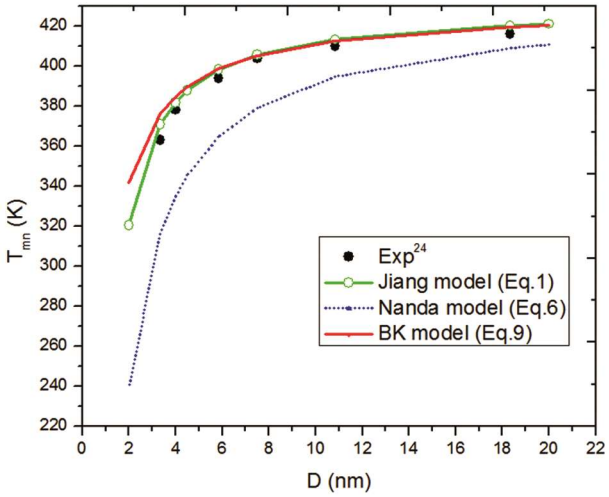

Fig. 5 – Size dependence of melting temperature for In (film).

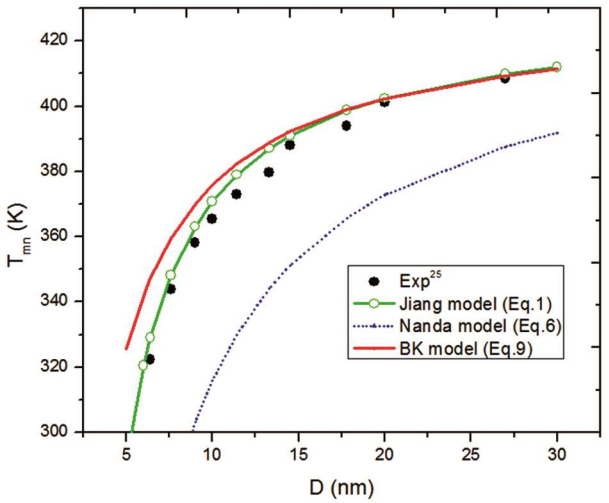

Fig. 6 – Size dependence of melting temperature for In (spherical).

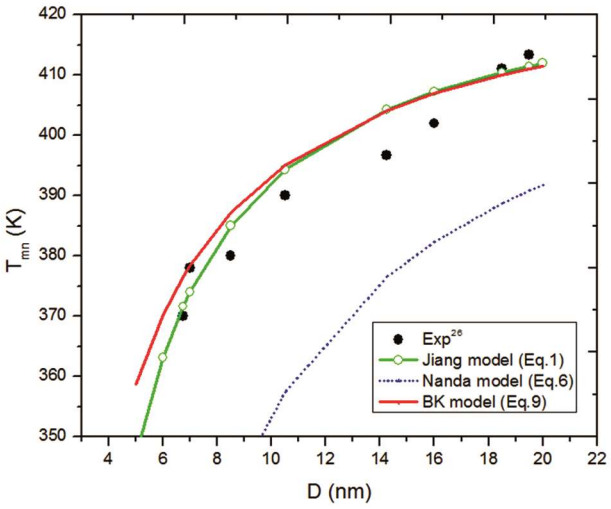

Fig. 7 – Size dependence of melting temperature for In (wire).

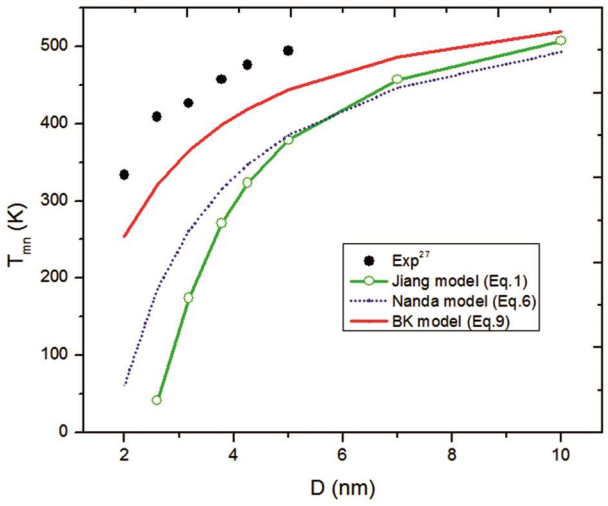

Fig. 8 – Size dependence of melting temperature for Pb (spherical).

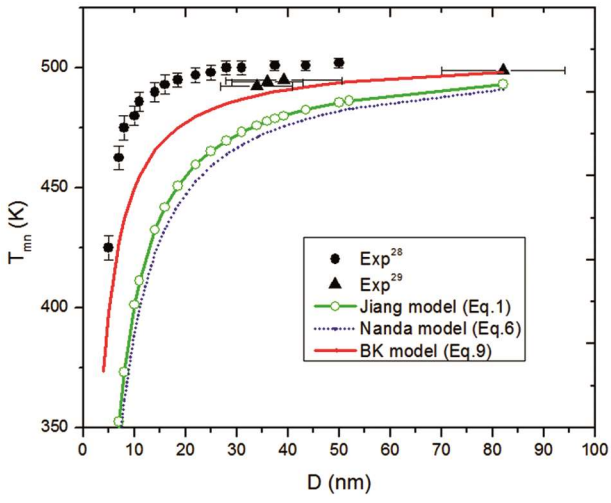

Fig. 9 – Size dependence of melting temperature for Sn (spherical).

increasing attention in the material science, since their properties are significantly different from those of either bulk material or a single molecule. The size dependent cohesive energy is the basic thermodynamic quantity, which determines other properties. It is well known that when size is reduced, the cohesive energy is increased[1,2,6] as discussed in detail by Zhu *et al.*[30] Moreover, the relation of cohesive energy (Eq. (8)) given by Nanda model implies that the cohesive energy per atom decreases as the particle size decreases[10]. The rate of decrease depends on the values of atomic volume and the coefficient of surface energy. Thus, Nanda model[10] gives reverse trends of variation for size dependence of cohesive energy as discussed above[30]. Now, there remain two models, viz. Jiang model and BK model which are used in the present paper to study the size dependence of cohesive energy. For this purpose, we have selected Al, Mo and w nanoparticles because of the fact that for these materials, experimental data are available so that the model predictions may be judged. We used Eq. (5) and Eq. (10) to compute the size dependence of cohesive energy which corresponds to Jiang model and BK model, respectively. The results obtained are reported in Figs 10-12. It is observed that both the formulations give the similar trends of variation. Moreover, the results obtained by BK model Eq. (10) are in better agreement with the experimental data[30,31] as compared with Jiang model Eq. (5). Due to the simplicity and applicability of BK model, we extended the same to study size dependence of Debye temperature. This gives Eq. (13). In the present paper, we used Eq. (13) to study.

Table 2 – Performance of different models for size dependence of melting temperature.

Material	Shape	Jiang model Eq. (1)	Nanda model Eq. (6)	BK model Eq. (9)
Ag	Spherical	×	✓	✓
Al	Spherical	×	✓	✓
Au	Spherical	×	✓	✓ ✓
Bi	Spherical	×	✓	✓
In	Film	✓	× ×	✓
In	Spherical	✓	×	✓
In	Wire	✓	× ×	✓
Pb	Spherical	×	×	✓
Sn	Spherical	×	×	✓

✓ demonstrates the good performance of the model and

× demonstrates poor performance of the model in the light of experimental data.

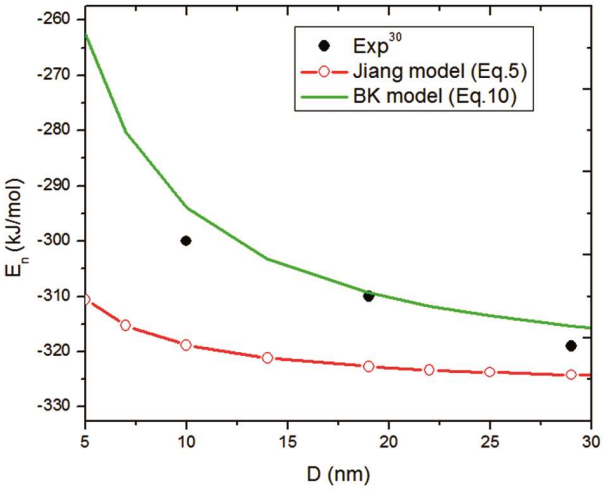

Fig. 10 — Size dependence of cohesive energy for Al (spherical)

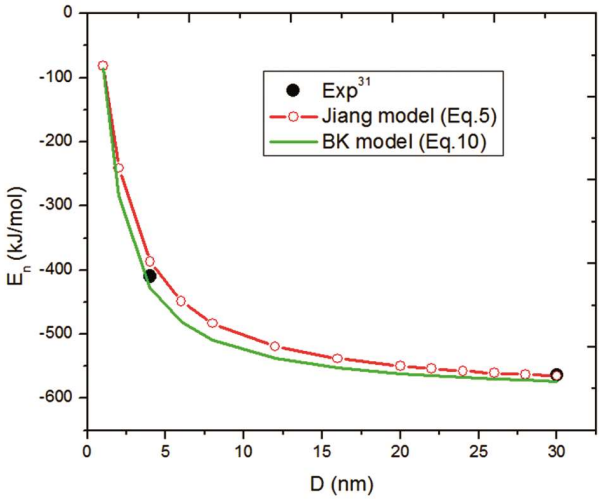

Fig. 11 – Size dependence of cohesive energy for Mo (spherical)..

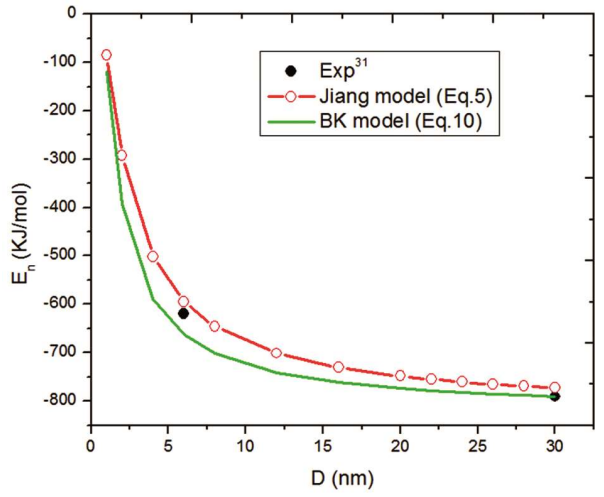

Fig. 12 – Size dependence of cohesive energy for W (spherical).

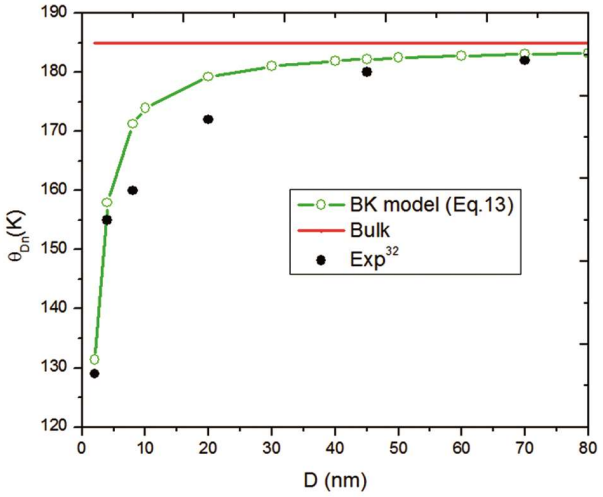

Fig. 13 – Size dependence of Debye temperature for Au (spherical).

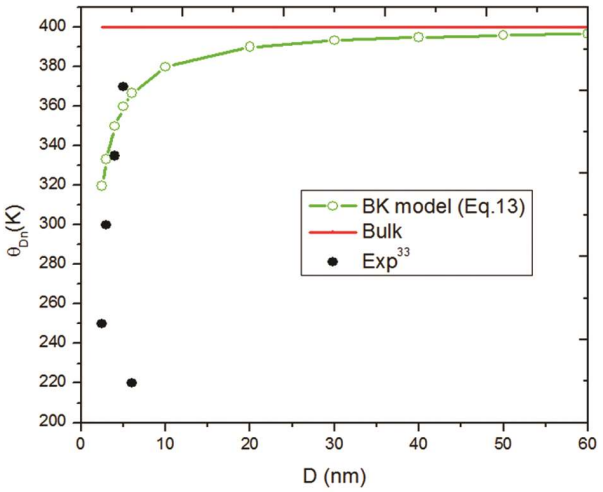

Fig. 14 – Size dependence of Debye temperature for Co (spherical).

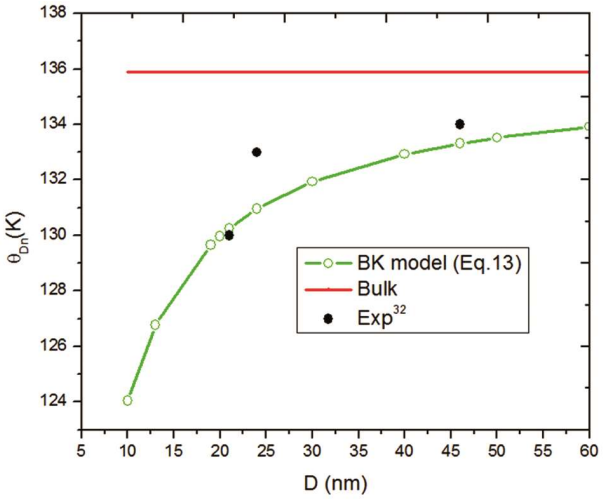

Fig. 15 – Size dependence of Debye temperature for Se (spherical).

the size dependence of Debye temperature of Au, Co and Se nanomaterials. The results obtained are reported in Figs (13-15) along with the available experimental data. A good agreement between theory and experiment demonstrates the validity of the model proposed for the size dependence thermodynamic properties of nanomaterials[32,33].

4 Conclusions

It is concluded that the applicability of Jiang model or Nanda model for the size dependence of melting temperature depends on the material considered. However, BK model has been found to work well for all the nanomaterials considered in the present paper. The model is further extended for the size dependence of cohesive energy and Debye temperature. A good agreement between the model predictions and experimental data support the validity of the model developed.

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