High Temperatures-High Pressures, Vol. XX, pp. 1–17
Reprints available directly from the publisher
Photocopying permitted by license only

Analysis of modified Gibbs-Thomson equation for size and shape dependence properties of nanomaterials

PRIYA PANERU AND MUNISH KUMAR

Department of Physics, G. B. Pant University of Agriculture and Technology, Pantnagar-263145, India

Recieved: March 29, 2024; Accepted: May 31, 2024.

A critical analysis of two phase (solid- liquid) model of melting temperature viz. modified Gibbs-Thomson equation is presented. The application of model is discussed for the size dependent properties of metallic nanocrystals. Melting temperature, cohesive energy, Debye temperature, specific heat, thermal conductivity and electrical conductivity are discussed. Some other formulations based on the bond energy model are also included for comparison purposes. The results are discussed in the light of available experimental data. The simplicity and applicability of the models is discussed along with the modified Gibbs-Thomson model.

Keywords: Size, shape, melting temperature, Debye temperature, specific heat

1 INTRODUCTION

Nanomaterials are a class of materials that possess unique properties due to their nanoscale size and structure. These materials can be engineered or naturally occurring and include different shapes. At the nanoscale, materials exhibit novel properties, such as enhanced surface area, quantum effects, and improved mechanical, electrical, or catalytic characteristics [1]. Nanoscience is an interdisciplinary field that explores and investigates phenomena at the nanoscale. It draws knowledge and expertise from various disciplines. Nano scientists study the fundamental principles governing the behaviour of matter

Corresponding authors: priyapaneru02@gmail.com; munish_dixit@yahoo.com

at the nanoscale. This knowledge forms the foundation for advancements in nanotechnology and guides researchers in harnessing these phenomena for practical applications [2]. It involves manipulating matter at the atomic or molecular scale to achieve specific functionalities with diverse applications. A careful review of literature shows that the properties of nanomaterials depend on size and shape [3, 4]. A lot of experimental [5–10] work has been done to understand the behaviour of nano materials in addition to the theoretical work [11–14, and references therein].

It has been observed that the melting temperature of nanoparticle decreases as decrease in the particle size. Three different models viz. Nanda model [15] Jiang model [16] and BK model [17] with different physical origin have been used to study the size dependence of melting temperature and cohesive energy of nanomaterials. A detailed analysis demonstrates that the Jiang model or Nanda model depends on the material considered [18]. Moreover, BK model [17] works well for the different nanomaterials.

An analytical model of melting temperature has been used by Ansari [19] based on the modified Gibbs–Thompson equation (William Thompson later became Lord Kelvin). Ansari [19] studied size-dependent thermodynamic properties of nanomaterials such as cohesive energy, melting temperature, Debye temperature, specific heat capacity, thermal and electrical conductivity. An excellent agreement with experimental data has been shown without considering earlier models, though they exist [15–17]. Thus, it is legitimate and may be useful to present a critical analysis of different models with their predicting powers in the light of available experimental data, which is the purpose of present paper. The effect of shape is also very useful for nano materials, therefore it is included in the present paper.

2 THEORETICAL FORMULATIONS

Melting is a very common phenomena in nature. Different theories of melting have been reviewed by Shankar and Kumar [20]. According to the thermodynamic theory, the melting point is a thermodynamic property [20], which may be described by the size dependence of molar Gibbs- energy [21, 22]. Qi [3, 4] developed a very simple theory based on the bond energy model to describe the melting temperature of free standing nanosolids. The results were reported for Sn and Pb nanoparticles and In (nanowire and nanofilm). The model has been further modified by Bhatt and Kumar [17] for its wide applicability. The detailed analysis is available elsewhere [17] and mathematical form of size and shape dependence of melting temperature reads as follows [17].

$$\frac{T_m(n)}{T_m(b)} = \left(1 - \frac{N}{2n}\right)^k \tag{1}$$

where $T_m(n)$ and $T_m(b)$ are the melting temperatures of nano and bulk materials respectively. n is the total number of atoms of a nanosolid and N the surface atoms. k is dimension less parameter with its value 2 as discussed in detail by Bhatt and Kumar [17]. It has also been discussed that Eq. (1) reduces to the relation as given by Qi [3, 4] for k = 1, which reads as follows [17]

$$\frac{T_m(n)}{T_m(b)} = \left(1 - \frac{N}{2n}\right) \tag{2}$$

Eq. (1) provides the simple method to understand the size and shape dependence of melting temperature as demonstrated in the recent literature [17]. Recently, Ansari [19] advocated a theoretical two-phase (solid-liquid) model of melting temperature based on modified Gibbs-Thomas Equation. This gives the following relation for melting temperature [19]

$$\frac{T_m(n)}{T_m(b)} = \left[1 - \frac{A_{sp.} V_m (\gamma_{sg} - \gamma_{lg})}{\Delta_m H_m^0}\right] \tag{3}$$

Here, V_m is molar volume γ_{sg} is surface energy, γ_{lg} the surface tension and $\Delta_m H_m^0$ enthalpy of fusion and Asp is 6/D for spherical nanoparticles, where D is the diameter. Thus, Eq. (3) has been used for spherical nanoparticle [19] as given below

$$\frac{T_m(n)}{T_m(b)} = \left[1 - \frac{6 V_m (\gamma_{sg} - \gamma_{lg})}{D \Delta_m H_m^0}\right] \tag{4}$$

It should be mentioned that in Eq. (3–4) the role of solid/liquid interfacial energy is neglected as discussed earlier [23, 24]. We have also neglected that the phase rule is changed in nanomaterials [25] i.e., we have one more freedom. That is why solidus and liquidus lines may be separated even in one component system [23, 26].

It has been discussed that different properties of nanomaterials may be derived from the knowledge of melting temperature [27–28]. Thus, the size dependence of melting temperature with shape plays an important role while describing the nanoscience. The most important is the cohesive energy, which is related with melting temperature as follows [29–30]

$$\frac{T_m(n)}{T_m(b)} = \frac{E(n)}{E(b)} \tag{5}$$

where, E(n) and E(b) are the cohesive energies of nano and bulk materials respectively. According to the bond energy model as proposed by Qi [3, 4] the cohesive energy reads as follows

$$\frac{E(n)}{E(b)} = \left(1 - \frac{N}{2n}\right) \tag{6}$$

Using Eq. (1) and Eq. (5) gives the following relation for cohesive energy

$$\frac{\mathrm{E(n)}}{\mathrm{E(b)}}=\left(1-\frac{\mathrm{N}}{2\mathrm{n}}\right)^{\mathrm{k}} \tag{7}$$

Using Eq. (3) and Eq. (5) gives the following relation for cohesive energy as used by Ansari [19]

$$\frac{\mathrm{E(n)}}{\mathrm{E(b)}}=\left[1-\frac{6V_m(\gamma_{sg}-\gamma_{lg})}{D\Delta_m H_m^0}\right] \tag{8}$$

Debye temperature is related to the highest normal mode of vibration of a crystal. It has been discussed that Debye temperature and melting temperature of nanomaterials are related as [31]

$$\frac{\theta_{\mathrm{D}}(\mathrm{n})}{\theta_{\mathrm{D}}(\mathrm{b})}=\left[\frac{\mathrm{T_m(n)}}{\mathrm{T_m(b)}}\right]^{1/2} \tag{9}$$

where $\theta_{\mathrm{D}}(\mathrm{n})$ and $\theta_{\mathrm{D}}(\mathrm{b})$ are the Debye temperatures of nanomaterial and bulk material respectively. Using Eq. (1) and Eq. (9) gives the following relation

$$\frac{\theta_{\mathrm{D}}(\mathrm{n})}{\theta_{\mathrm{D}}(\mathrm{b})}=\left(1-\frac{\mathrm{N}}{2\mathrm{n}}\right) \tag{10}$$

and Eq. (2) and Eq. (9) gives

$$\frac{\theta_{\mathrm{D}}(\mathrm{n})}{\theta_{\mathrm{D}}(\mathrm{b})}=\left(1-\frac{\mathrm{N}}{2\mathrm{n}}\right)^{1/2} \tag{11}$$

similarly, Eq. (4) and Eq. (9) gives the following relation as presented by Ansari [19]

$$\frac{\theta_{\mathrm{D}}(\mathrm{n})}{\theta_{\mathrm{D}}(\mathrm{b})}=\left[1-\frac{6V_m(\gamma_{sg}-\gamma_{lg})}{D\Delta_m H_m^0}\right]^{1/2} \tag{12}$$

Zhu *et al*. [32] discussed that the specific heat (C) of bulk material is inversely proportional to the square of Debye temperature $\left(C\propto\frac{1}{\theta_D^2}\right)$ and the approximation is valid for nanomaterials also. This gives the following relation [32]

$$\frac{\mathrm{C(n)}}{\mathrm{C(b)}}=\left[\frac{\theta_{\mathrm{D}}(\mathrm{b})}{\theta_{\mathrm{D}}(\mathrm{n})}\right]^2 \tag{13}$$

Eq. (10) and Eq. (13) give the following relation for specific heat

$$\frac{C(n)}{C(b)} = \left(1 - \frac{N}{2n}\right)^{-2} \tag{14}$$

Singh et al [33] used the above discussed approximation in Eq. (11) and Eq. (13) which gives the following relation

$$\frac{C(n)}{C(b)} = \left(1 - \frac{N}{2n}\right)^{-1} \tag{15}$$

Eq. (15) has been used by Singh et al [33] and claimed to be derived by them, in spite of the derivation of Eq. (11) already available [34].

Combining Eq. (12) and Eq. (13) gives the following relation as reported by Ansari [19]

$$\frac{C(n)}{C(b)} = \left[1 - \frac{6V_m(\gamma_{sg} - \gamma_{lg})}{D\Delta_m H_m^0}\right]^{-1} \tag{16}$$

Now, we proceed to discuss the size and shape dependence of the thermal conductivity. The kinetic theory of solids gives the following relation [33, 35]

$$\frac{K(n)}{K(b)} = \frac{C(n)V(n)l(n)}{C(b)V(b)l(b)} \tag{17}$$

K(n), V(n), l(n) are the thermal conductivity, average phonon velocity, mean free path of nanomaterials and K(b), V(b), l(b) are corresponding to bulk material. Singh et al [33] as well as Ansari [19] assumed that specific heat is independent of size. It is well known [36] that

$$\frac{l(n)}{l(b)} = \frac{T_m(n)}{T_m(b)} \tag{18}$$

and

$$\frac{V(n)}{V(b)} = \left(\frac{T_m(n)}{T_m(b)}\right)^{1/2} \tag{19}$$

Thus

$$\frac{K(n)}{K(b)} = \left(\frac{T_m(n)}{T_m(b)}\right)^{3/2} \tag{20}$$

Singh et al [37] reported the following relation, using Eq. (2) and Eq. (20)

$$\frac{K(n)}{K(b)} = \left(1 - \frac{N}{2n}\right)^{3/2} \tag{21}$$

and Ansari [19] used Eq. (3) and Eq. (20) to get the following relation

$$\frac{\mathrm{K(n)}}{\mathrm{K(b)}} = \left[1 - \frac{6V_m(\gamma_{sg} - \gamma_{lg})}{D\Delta_m H_m^0}\right]^{3/2} \tag{22}$$

Ansari [19] assumed that the size effect on thermal conductivity is equivalent to that in electrical conductivity, which gives

$$\frac{\sigma(\mathrm{n})}{\sigma(\mathrm{b})} = \frac{\mathrm{K(n)}}{\mathrm{K(b)}} \tag{23}$$

where $\sigma(n)$ is the electrical conductivity of nanomaterial and $\sigma(b)$ for the corresponding bulk material. Ansari [19] discussed that Eq. (22) and Eq. (23) give following relation

$$\frac{\sigma(n)}{\sigma(b)} = \left(1 - \frac{A_{sp.}V_m(\gamma_{sg} - \gamma_{lg})}{\Delta_m H_m^0}\right)^{3/2} \tag{24}$$

For spherical nanoparticle

$$\frac{\sigma(\mathrm{n})}{\sigma(\mathrm{b})} = \left(1 - \frac{6V_m(\gamma_{sg} - \gamma_{lg})}{D\Delta_m H_m^0}\right)^{3/2} \tag{25}$$

The results based on Eq. (25) for Cu spherical nanoparticle viz. size dependence of electrical conductivity as reported by Ansari [19] are discussed below.

3 RESULTS AND DISCUSSION

A critical analysis is presented for the size dependence of different properties of nano materials viz. melting temperature, cohesive energy, Debye temperature, specific heat, thermal conductivity and electrical conductivity. For further understanding, the shape dependence of some properties are also presented as examples. A two phase (solid-liquid) model of melting temperature viz. modified Gibbs-Thomson Equation as used by Ansari [19] is critically examined along with some earlier models viz. Qi [3, 4] and BK [17]. The input parameters used in the present work have taken from Ansari [19] so that a comparison can be presented. The size dependence of melting temperature of Ag (spherical) nanomaterial using Eqs. (1–3) is reported in Fig. 1 along with available experimental data. It is found that Eq. (2) gives some higher values whilst Eq. (3) gives some smaller values as compared with the available experimental information. Moreover, the results obtained by Eq. (1) are in good agreement with the available experimental data [6]. This clearly demonstrates the superiority of Eq. (1) as compared to Eq. (2) and Eq. (3). The size dependence of cohesive energy of Molybdenum (Mo) and Tungsten (W) nano materials using Eqs. (6–8) is reported in Fig. 2 and

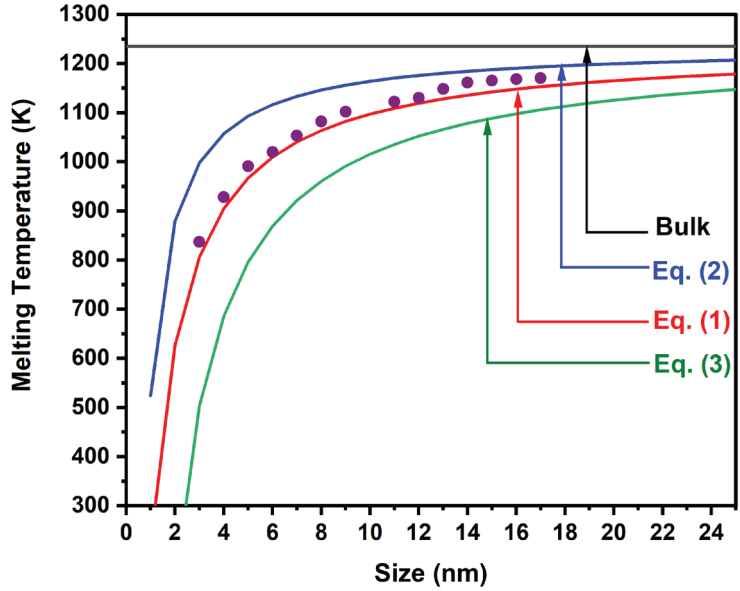

FIGURE 1
Effect of size on melting temperature of Ag (spherical) nanomaterial, • represent experimental data [6].

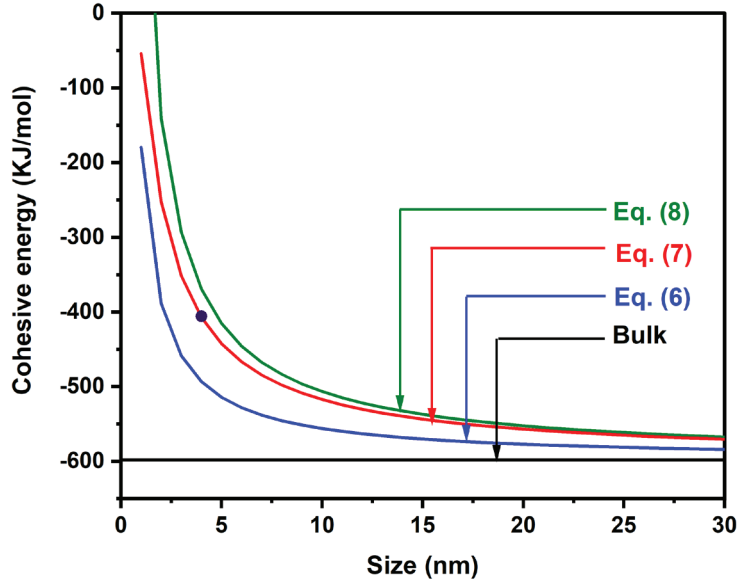

FIGURE 2
Effect of size on cohesive energy of Mo (spherical) nanomaterial, • represent experimental data [7].

Fig. 3 along with the available experimental data [7]. It is found that Eq. (8) gives some higher values while Eq. (6) gives some smaller values as compared with the available experimental data. Moreover, the results obtained by Eq. (7) are in good agreement with available experimental data. This clearly demonstrates the suitability of Eq. (7) as compared to Eq. (6) and Eq. (8). The size dependence of Debye temperature (θ_D) of Silver (Ag) and Cobalt (Co) nano materials using Eqs. (10–12) is reported in Fig. 4 and Fig. 5 along with the available experimental data [5, 8]. It is found that Eq. (11) gives some higher values while Eq. (12) gives some smaller values. Moreover, the results obtained by Eq. (10) are in good agreement with available experimental data [8] in smaller size range.

The size dependence of specific heat of Silver (Ag) nano material using Eqs. (14–16) is reported in Fig. 6 along with the available experimental data [9, 10]. Different formulations give the similar trends of variations. Moreover, the results obtained from Eq. (14) are in good agreement with available experimental data [9, 10]. This clearly demonstrates the superiority of Eq. (14). These models for specific heat show that specific heat varies with size at low dimension, although it becomes constant at higher size. The increase of Cn/Cb indicates that specific heat is inversely related to the grain size. Actually, the main reason of the elevated specific heat at small size is large atomic thermal vibration energy of surface atoms [19, 38]. Luo et al [9] remarked this discrepancy between bulk and nanomaterials in terms of surface free energy.

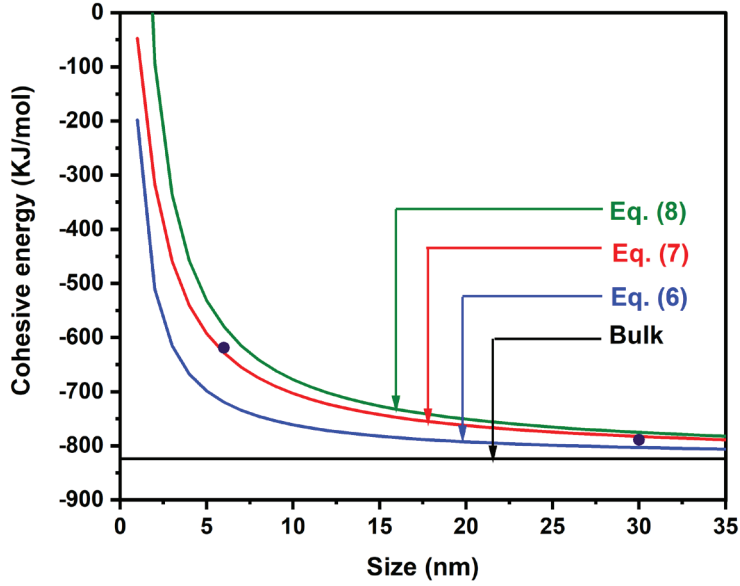

FIGURE 3
Effect of size on cohesive energy of W (spherical) nanomaterial, • represent experimental data [7].

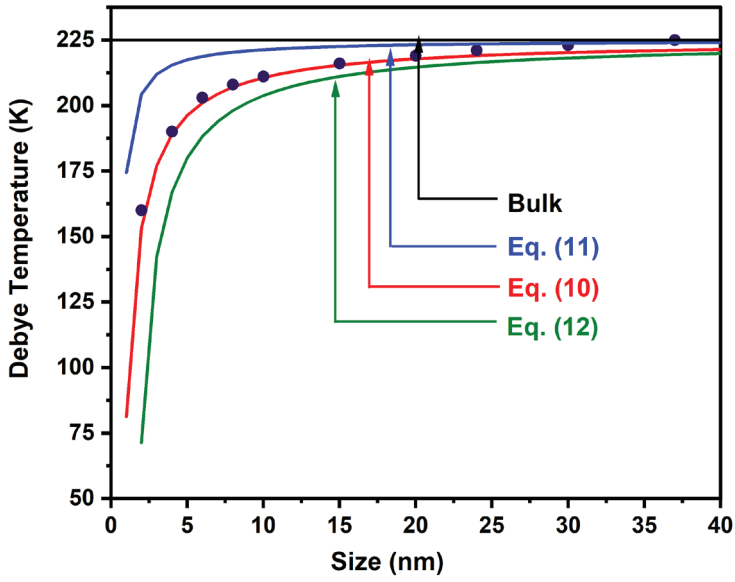

FIGURE 4
Effect of size on Debye temperature of Silver (spherical) nanomaterial, • represent experimental data [5].

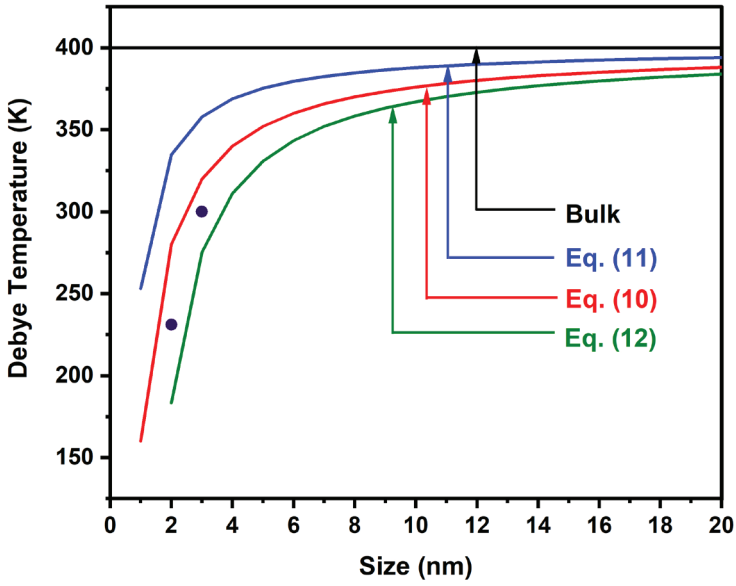

FIGURE 5
Effect of size on Debye temperature of Co (spherical) nanomaterial, • represent experimental data [8].

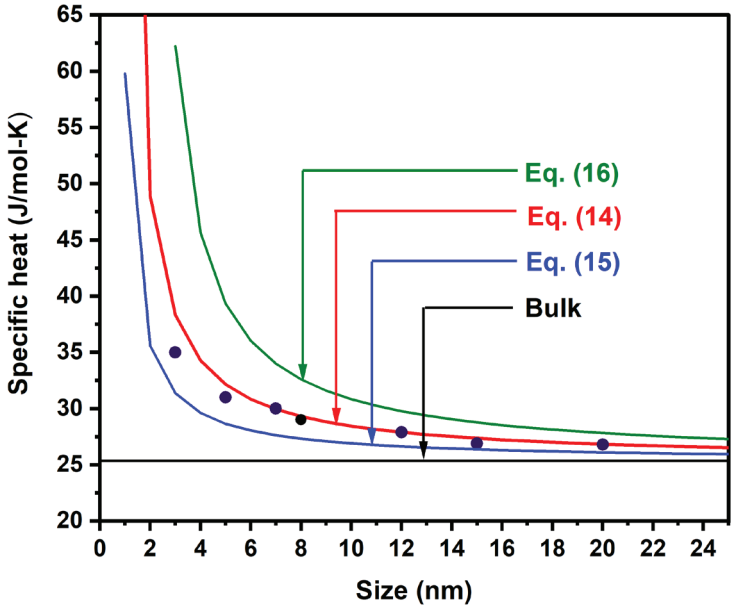

FIGURE 6
Size dependence of specific heat of Silver (spherical) nanomaterial, • represent experimental data [9, 10].

Singh et al [33] as well as Ansari [19] assumed that the specific heat is independent of size and reported Eq. (21) and Eq. (22). These Eqs. (21, 22) have been used to predict the size dependence of thermal conductivity [19, 33], which needs a deep discussion. Let us first look into the work of same authors [19, 37]. Singh et al [37] wrote "We assumed that the specific heat is constant" and Ansari [19] also used this while deriving Eq (22). Contrary to this, these authors [19, 37] reported the size dependence of specific heat (Refer to Figs. 1 to 4 of Singh et al [37] and Fig.6 of Ansari [19]). Thus, their statements are not justified. Further to test this we can proceed with available experiment data as discussed below.

Liu and Asheghi [39] measured the thermal conductivity and wrote "Thermal conductivity of 20 nm thick silicon layer is ∼22 W/mK". However thermal conductivity computed using Eq. (21) is 146.3W/mk, which is in ∼565% error with experimental data [39]. Moreover, a good agreement has been shown by Singh et al [37] for Si thin film. Ansari [19] used Eq. (22) to predict the thermal conductivity of spherical Ag nanoparticle and reported a good agreement with experiment data as reported by Warrier and Teja [40]. It should be mentioned that Warrier and Teja [40] reported the thermal conductivity of nanofluid consisting of silver nanoparticle dispersed in ethylene glycol. Thus, neither these results [40] match with Eq. (22) nor reasonable for Ag (spherical) as used by Ansari [19] for comparison purposes. Thus, it may be concluded that the size independence nature of specific heat for

nanomaterials as considered earlier [19, 33] is not justified. It should be taken size dependence [36] for small nanorange.

Bhatt and Kumar [36] considered the size dependence of specific heat in bond energy model. This gives the simple formulation of thermal conductivity of nanoparticle. The theory thus proposed gives the good agreement with the available experiment data. The results have also been compared with the Eq. (21) as used by Singh et al [37] which is similar to the Eq. (22). It should be mentioned that Eq. (22) replaces the term N/2n by $\left(\frac{A_{sp.} V_m (\gamma_{sg} - \gamma_{lg})}{\Delta_m H_m^0}\right)$ of Eq. (21). Using the size independence nature of specific heat, Ansari [19] extended the model of thermal conductivity to get relation of electrical conductivity (Eq. 25). The formulation has been used to predict the size dependence of electrical conductivity of Cu spherical nanoparticle (Ref. to Fig. 5 of [19]). The results show good agreement with experimental data from Nath and Chopra [41]. It is pertinent to discuss here that Nath and Chopra [41] reported the thermal conductivity of Cu film. These authors [41] neither reported the experimental results for Cu spherical nor electrical conductivity. Thus, the model predictions (Eq. 25) are not supported by experimental data [41]. This demonstrates that the size independent nature of specific heat for nanomaterials is not justified.

The shape effect also plays an important role in describing the behavior of nanomaterials in addition to the size effect. It seems that the formulation based on the BK model (Eq. 1) performs well as compared with the other relations reported in the literature. We have therefore extended the application of BK model to the study the shape dependence of melting temperature, cohesive energy, Debye temperature and specific heat. The formulations for this purpose have been obtained by putting the values of $\frac{N}{2n}$ from Table 1 in the corresponding equations. The results obtained are summarized in Figures 7–12. This shows that the properties considered in the present paper

TABLE 1
The values of $\frac{N}{2n}$ as reported by Bhatt and Kumar [17] and other input parameters from Ansari [19].

Shape	**N/2n**
Film	0.666 d/h
Dodecahedral	0.898 d/*a*
Icosahedral	1.323 d/*a*
Wire	1.333 d/L
Spherical	2 d/D
Hexahedral	2d/*a*
Octahedral	2.449 d/*a*
Tetrahedral	4.898 d/*a*

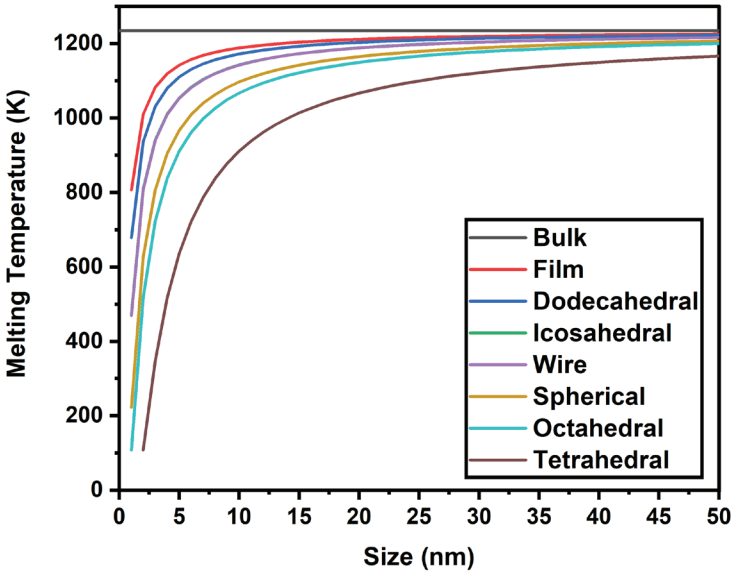

FIGURE 7
Shape dependence of melting temperature for Ag (spherical) nanomaterial using Eq. (1).

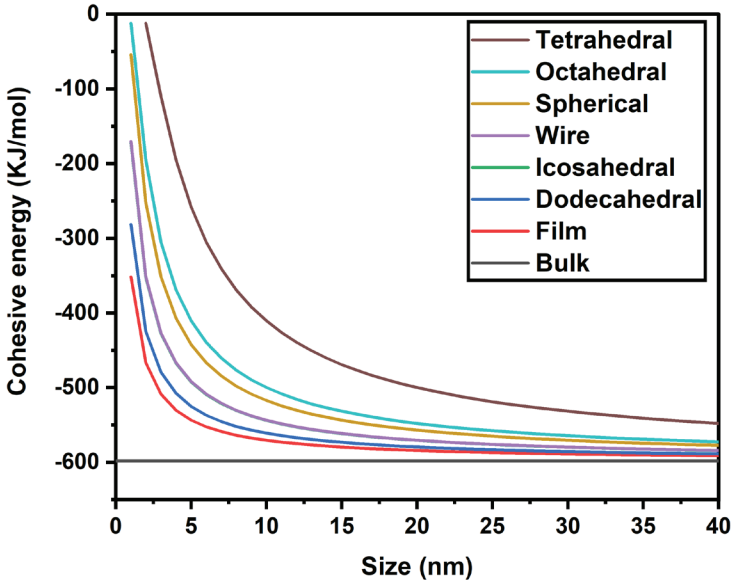

FIGURE 8
Shape dependence of cohesive energy for Mo (spherical) nanomaterial using Eq. (7).

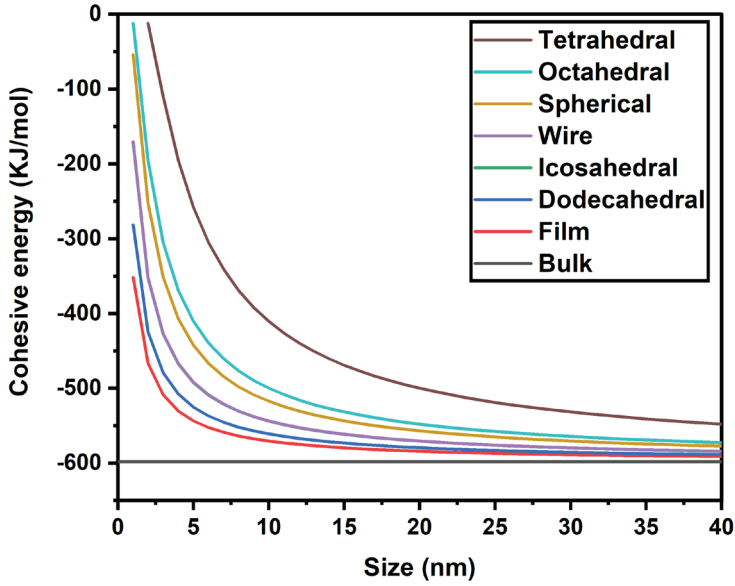

FIGURE 9
Shape dependence of cohesive energy for W (spherical) nanomaterial using Eq. (7).

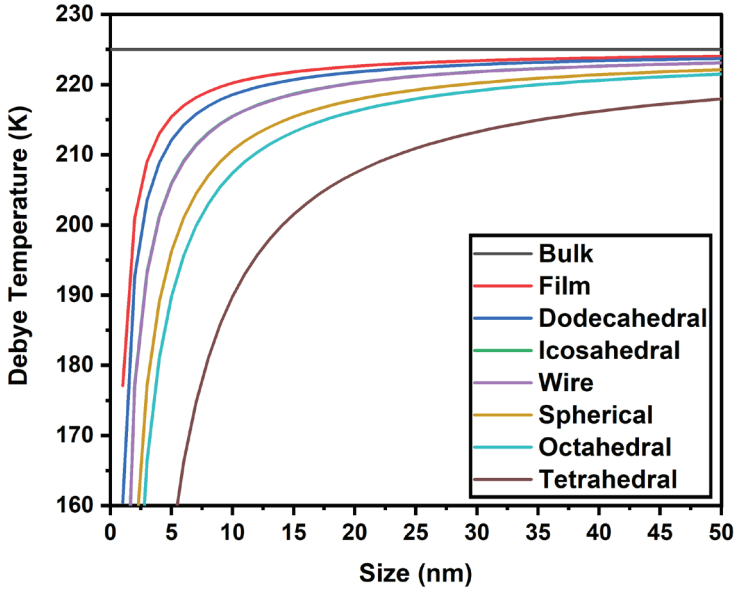

FIGURE 10
Shape dependence of Debye temperature for Silver (spherical) nanomaterial using Eq. (10).

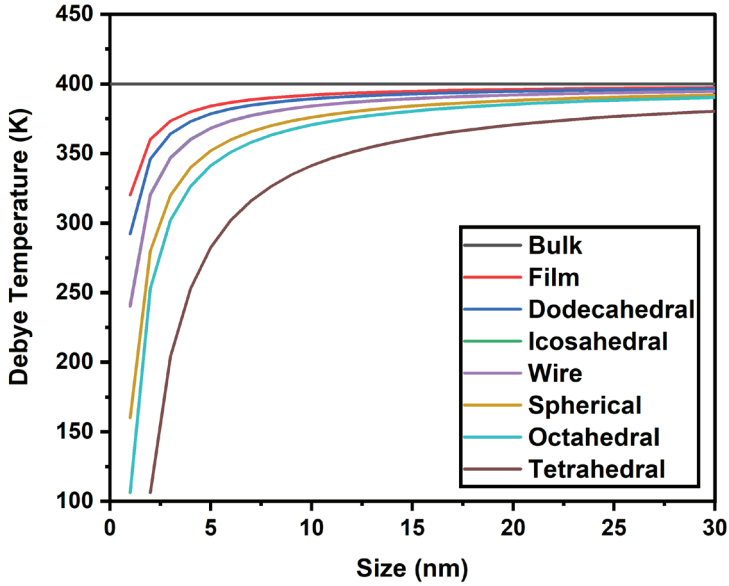

FIGURE 11
Shape dependence of Debye temperature for Co (spherical) nanomaterial using Eq. (10).

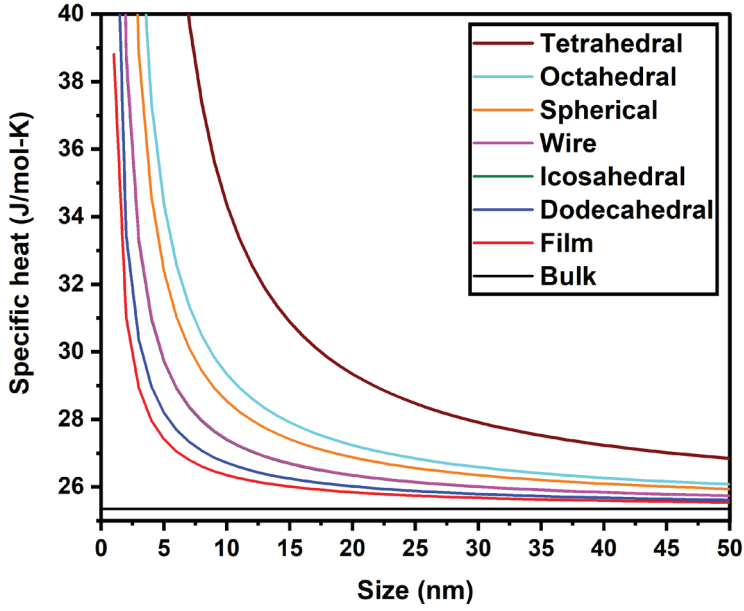

FIGURE 12
Shape dependence of specific heat for Silver (spherical) nanomaterial using Eq. (14).

depends on the shape also in addition to size. Actually, the purpose of present paper is to introduce the simplicity in the more complicated phenomena of nanoscience. The model developed in the present paper has been used to understand the effect of size and shape of independent nano-particles, levitating in space. Due to simplicity and applicability, the model may be extended to different type of nanomaterials for their different properties. These, may be size dependence of heat conductivity of composite materials, nanoparticles in multi-phase situation, size dependence of heat of mixing, size dependence of solubility [42–46] as our future research work.

4 CONCLUSIONS

We have thus presented a critical analysis of different theoretical models viz. Qi model as used by Singh et al. [33, 37], Ansari model [19] and BK model [17] to predict the size dependent properties of nanomaterials. These properties are melting temperature, cohesive energy, Debye temperature, specific heat, thermal conductivity and electrical conductivity. The reality of the models is discussed in the light of available experimental data. This may help the researchers to understand the size and shape dependent properties of nanomaterials in a suitable way.

ACKNOWLEDGEMENT

We are thankful to the reviewer for his valuable comments, which have been found very useful to revise the manuscript. One of us (P. Paneru) is also thankful to GBPUAT, Pantnagar for financial support during the present work.

REFERENCES

[1] Iijima, S. *nature*, **354** (1991), 56, https://doi.org/10.1038/354056a0
[2] Roco, M. C. J. Nanoparticle Research, 4 (2002), 9, https://doi.org/10.1023/A:1020157027792
[3] Qi, W. H. *Physica B,* **368** (2005), 46. https://doi.org/10.1016/j.physb.2005.06.035
[4] Qi, W. H. *Nanoscopic Thermodynamics Acc. Chem. Res.,* **49** (2016), 1587. https://doi.org/10.1021/acs.accounts.6b00205
[5] Sadaiyandi, K. *Materials Chem. Phys.,* **115** (2009), 703, https://doi.org/10.1016/j.matchemphys.2009.02.008
[6] Xiao, S., Hu, W., Yang, J. *J. Phys. Chem. B,* **109** (2005), 20339, https://doi.org/10.1021/jp054551t
[7] Kim, H. K., Huh, S. H., Park, J. W., Jeong, J. W., Lee, G. H. *Chem. Phys. Lett.,* **354** (2002), 165, https://doi.org/10.1016/S0009-2614(02)00146-X
[8] Hou, M., El Azzaoui, M., Pattyn, H., Verheyden, J., Koops, G., Zhang, G. *Phys. Rev. B,* **62** (2000), 5117, https://doi.org/10.1103/PhysRevB.62.5117
[9] Luo, W., Hu, W., Xiao, S. *J. Phys. Chem., C* **112** (2008), 2359, https://doi.org/10.1021/jp0770155

[10] Xiong, S., Qi, W., Cheng, Y., Huang, B., Wang, M., Li, Y. Phys. Chem. Chem. Phys., 13 (2011), 10652, https://doi.org/10.1039/C0CP90161J
[11] Kaptay, G. *J. Mater. Sci*., **47** (2012), 8320, https://doi.org/10.1007/s10853-012-6772-9
[12] Kaptay, G., Janczak-Rusch, J., Pigozzi G., Jeurgens, L. H. *J. Mater. Eng. Perform.* **23** (2014), 1600, https://doi.org/10.1007/s11665-014-0885-z
[13] Kaptay, G., Janczak-Rusch J., Jeurgens, L. P. H. *J. Mat. Eng Perform.* **25**, (2016), 3275, https://doi.org/10.1007/s11665-016-2123-3
[14] Kaptay, G. *J. Mat. Eng. Perform.,* **27** (2018), 5023, https://doi.org/10.1007/s11665-018-3411-x
[15] Nanda, K. K., Sahu, S. N. Behera, S. N. *Phys. Rev. A,* **66**, (2002), 013208, https://doi.org/10.1103/PhysRevA.66.013208
[16] Jiang, Q., Li, J. C., Chi, B. Q. *Chem Phys Lett.,* **366** (2002), 551, https://doi.org/10.1016/S0009-2614(02)01641-X
[17] Bhatt, S., Kumar, M. *J. Phys. Chem. Solids,* **106** (2017), 112, https://doi.org/10.1016/j.jpcs.2017.03.010
[18] Chbabra, H., Kumar, M., Bhatt, S. *Indian J. Pure and Appl. Phys*., **57** (2019), 361, http://op.niscpr.res.in/index.php/IJPAP/article/view/19341
[19] Ansari, A. M. *Appl. Phys. A* **385** (2021), 127, https://doi.org/10.1007/s00339-021-04535-4
[20] Shanker, J., Kumar, M. *Phys. Stat. Solidi (b)* **158** (1990), 11, https://doi.org/10.1002/pssb.2221580102
[21] Kaptay, G. *J. nanosci. Nanotech*., **12** (2012), 2625, https://doi.org/10.1166/jnn.2012.5774
[22] Kaptay, G. RSC Adv, **7** (2017), 41241, https://doi.org/10.1039/C7RA07911G
[23] Vegh A., Kaptay, G. *Calphad* **63** (2018), 37, https://doi.org/10.1016/j.calphad.2018.08.007
[24] Jin, B., Liu, S., Du, Y., Kaptay G., Fu T. *Phys. Chem. Chem. Phys.* 24 (2022), 22278, https://doi.org/10.1039/D2CP01931K
[25] Kaptay, G. *J. Nanosci. Nanotechnol.,* **10** (2010), 8164, https://doi.org/10.1166/jnn.2010.3047\
[26] Mei Q. S. Lu, K. *Prog. Mater. Sci.,* 52 (2007), 1175, https://doi.org/10.1016/j.pmatsci.2007.01.001
[27] Pandey, V., Kumar, M. *Physica B: Condensed Matter*, **629** (2022), 413617, https://doi.org/10.1016/j.physb.2021.413617
[28] Paneru, P., Kumar, M. *Modern Phys. Lett. B*, **37** (2023), 2350111, https://doi.org/10.1142/S0217984923501117
[29] Guisbiers, G. Res. Lett., 5 (2010), 1132, https://doi.org/10.1007/s11671-010-9614-1
[30] Guisbiers, G. Buchaillot, L. Phys. Lett. A, 374 (2009), 305, https://doi.org/10.1016/j.physleta.2009.10.054
[31] Kumar, R. Kumar, M. *Indian J. Pure and Appl. Phys.,* **51** (2013), 87, https://nopr.niscpr.res.in/bitstream/123456789/15911/1/IJPAP/2051(2)
[32] Zhu, Y. F. Lian, J. S. Jiang, Q. *J. Phys. Chem. C,* **113** (2009), 168966, https://doi.org/10.1021/jp902097f
[33] Singh, M., Lara, S., Tlali, S. *J. Taibah Uni. Sci.,* **11** (2017), 922, https://doi.org/10.1016/j.jtusci.2016.09.011
[34] Kumar, R. Kumar, M. *I*ndian J. Pure Appl. Phys., 50 (2012), 329, https://nopr.niscpr.res.in/bitstream/123456789/14004/1/IJPAP
[35] Kittel C. *Introduction to Solid State Physics*, 8th ed. New Delhi, John Wiley and Sons Inc; 2013, http://metal.elte.hu/~groma/Anyagtudomany/kittel
[36] Bhatt, S. Kumar, M. *Indian J. Pure Appl. Phys.,* **56** (2018), 210, http://op.niscpr.res.in/index.php/IJPAP/article/view/17360
[37] Singh, M. Hlabana, K. K. Singhal, S. K. Devlal, K. *J. Taibah Univ. Sci.*, **10** (2016), 375, https://doi.org/10.1016/j.jtusci.2015.04.006
[38] Rupp, J., Bringer, R. *Phys. Rev. B,* **36** (1987), 7888, https://doi.org/10.1103/PhysRevB.36.7888
[39] Liu, W. Asheghi, M. *Appl. Phys. Lett.,* **84** (2004), 3819, https://doi.org/10.1063/1.1741039
[40] Warrier, P., Teja, A. Nanoscale Res. Lett., **6**, (2011), 1, https://doi.org/10.1186/1556-276X-6-247
[41] Nath, P. Chopra, K. L. *Thin Solid Films*, **20** (1974), 53, https://doi.org/10.1016/0040-6090(74)90033-9

[42] Kaptay, G. *Int. J. Pharmaceutics,* **430** (2012), 253, https://doi.org/10.1016/j.ijpharm.2012.03.038
[43] Yakymovych, A., Sklyarchuk, V., Plevachuk Yu., Sokoliuk, B. *J. Phys. Chem. C,* **120** (2016), 1881, https://doi.org/10.1007/s11665-016-2297-8
[44] Yakymovych, A., Kaptay, G., Flandorfer, H., Bernardi, J., Schwarz S., Ipser, H. *RSC Adv.,* **8** (2018), 8856, https://doi.org/10.1039/C7RA13643A
[45] Kaptay, G. *Adv Colloid Interface Sci.,* **256** (2018), 163, https://doi.org/10.1016/j.cis.2018.04.007
[46] Wen, S., Du, Y., Tan, J., Liu, Y., Zhou, P., Long, J., Kaptay, G. *J Mater Sci & Technol.,* **97** (2022), 123, https://doi.org/10.1016/j.jmst.2021.04.036