

Size-dependent melting of nanoparticles: Hundred years of thermodynamic model*

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Abstract. Thermodynamic model first published in 1909, is being used extensively to understand the size-dependent melting of nanoparticles. Pawlow deduced an expression for the size-dependent melting temperature of small particles based on the thermodynamic model which was then modified and applied to different nanostructures such as nanowires, prism-shaped nanoparticles, etc. The model has also been modified to understand the melting of supported nanoparticles and superheating of embedded nanoparticles. In this article, we have reviewed the melting behaviour of nanostructures reported in the literature since 1909.

Keywords. Nanoparticles; melting; thermodynamic model.

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1. Introduction

It has been well established both experimentally and theoretically that the melting temperature (T_{cm}) of nanoparticles depends on the particle size [1–85]. However, Pawlow in 1909 developed a thermodynamic model [1], that predicts a melting point depression of nanoparticles and the variation is linear with the inverse of the particle size. An attempt to confirm this experimentally has been made first by Pawlow [2] in 1910. Subsequently, other researchers [3–30] have investigated the variation of melting temperature with particle size and many theoretical models [31–72] have successfully been applied to understand the size dependency of melting temperature.

Melting point depression occurs for almost all free nanoparticles [1–72] with anomaly in few cases [73–93]. The melting temperature higher than that of bulk

*This article is dedicated to Indian Institute of Science which is also celebrating its centenary this year.

– a phenomenon called superheating – has also been reported for some cases. Superheating has been reported for nanoparticles embedded in other host materials [73–85] such as Pb nanoparticles in Al host, In nanoparticles in Al host, Ge in SiO₂ host, etc. Thermodynamic model has been modified to understand the superheating of embedded nanoparticles [77].

The melting temperature of inert gas (neon, argon, krypton, xenon) nanoparticles also decreases with decreasing particle size [42,94–98]. Though the depression of the melting temperature has been reported for inert gas nanoparticles in porous glasses [94–98], superheating has also been reported when embedded in Cu, Ni and Al matrices [99,100]. According to different theoretical models, the variation is linear with the inverse of the particle size for large nanoparticles and deviates from the linearity for small nanoparticles [42,97,98].

Some anomaly in the melting behaviour of free nanoparticles has also been reported [73–93]. The melting of Ga and Sn clusters occurs at a higher temperature as compared to the bulk [86,87]. This is thought to be due to the structural difference or the difference in bonding [88,89]. Local maxima and minima in the melting temperature have been reported for Na, Al and Ar clusters and are expected to be due to structural effect [91–93].

Though there are several theoretical models [31–72], thermodynamic model has lots of merits over other models and has been used by many researchers to understand their experimental results:

1. Different researchers have observed different variations of melting temperature even for the same material which can be predicted easily by thermodynamic model. Different expressions can be derived by assuming different melting hypothesis that explains different variations.

2. The model can be used to understand the size-dependent melting of non-spherical nanoparticles such as prism-shaped, decahedral, pyramidal etc. along with nanowires and thin films.

3. The model is consistent with molecular dynamic (MD) simulations.

Therefore, it is necessary to acquire more information about the thermodynamic model. In this article, we have compiled the important issues on thermodynamic model and the size-dependent melting of nanoparticles for the past hundred years. While completeness is a much-desired goal, it would be surprising if some deserving papers have not been omitted in the course of looking back over a 100-year period. Nevertheless, I have tried my best to provide a wealth of information through this review article.

2. Thermodynamic model and different hypotheses

There are different melting processes as demonstrated in figure 1. In one of the process, the entire solid is in equilibrium with entire melted particles [1,15] which corresponds to homogeneous melting hypothesis (HMH). There is no surface melting for such a case and the melting temperature T_{cm} of nanoparticles can be expressed as [15]

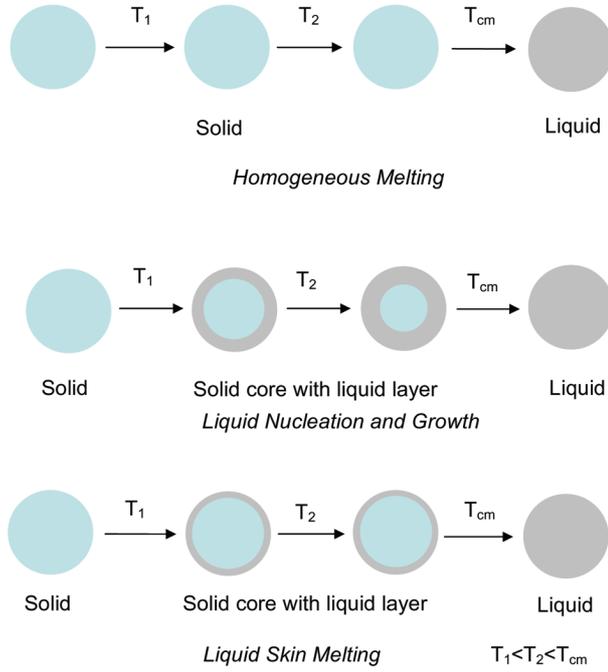


Figure 1. Three different melting hypotheses for nanoparticles.

$$\frac{T_{cm}}{T_{CM}} = 1 - \frac{4V}{\Delta H_f D} \left[\gamma_{sv} - \gamma_{lv} \left(\frac{\rho_s}{\rho_l} \right)^{2/3} \right] = 1 - \frac{\beta_{HMH}}{D}, \quad (1)$$

where γ_s are surface energies of solid–vapour and liquid–vapour interfaces of the material, ΔH_f is the bulk latent heat of fusion, D is the diameter of nanoparticles, ρ_s and ρ_l are the densities of solid and liquid and T_{CM} is the bulk melting temperature.

Another process that corresponds to liquid skin melting (LSM) is known to prevail for some cases [6,30]. LSM considers the formation of a liquid layer over the solid core at a low temperature that remains unchanged till the particle transforms completely to liquid at the melting temperature. The expressions for T_{cm} is given by

$$\frac{T_{cm}}{T_{CM}} = 1 - \frac{4\gamma_{sl}V}{\Delta H_f(D - 2\delta)} = 1 - \frac{\beta_{LSM}}{D - 2\delta}. \quad (2)$$

It may be noted that eq. (3) predicts a faster variation with respect to the inverse of the particle size and the melting temperature is non-linear.

In another process that corresponds to liquid nucleation and growth (LNG) [22,32,33,38], a liquid layer nucleates and grows with temperature. This corresponds to surface melting and the melting temperature can be given by

$$\frac{T_{cm}}{T_{CM}} = 1 - \frac{6V}{\Delta H_f D} \left[\gamma_{sv} - \gamma_{lv} \left(\frac{\rho_s}{\rho_l} \right)^{1/2} \right] = 1 - \frac{\beta_{LNG}}{D}. \quad (3)$$

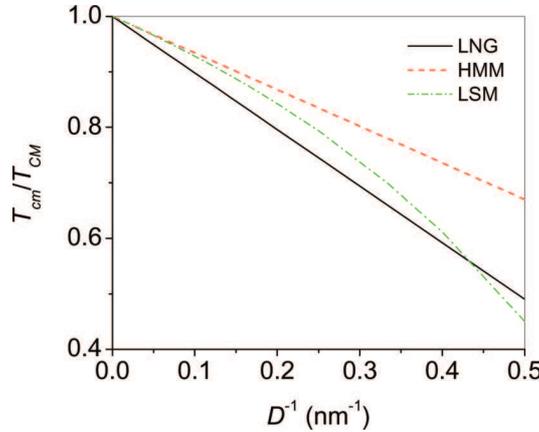


Figure 2. Comparison of melting temperature according to HMM, LNG and LSM.

It may be noted from eqs (1) and (2) that both HM and LNG predict a linear variation of melting temperature with the inverse of size. The difference between eqs (1) and (2) is the pre-factor. Many researchers have also derived eq. (2) and most of the experimental data have been analysed by eq. (2) where γ_{sv} is adjusted to fit the experimental data [12,16].

The coefficients of eqs (1)–(3) are related as $\gamma_{sl} \sim (\gamma_{sv} - \gamma_{lv})$. Based on equations (1)–(3), the melting temperature of nanoparticles can be represented by

$$1 - \frac{T_{cm}}{T_{CM}} = \frac{z\beta}{D - 2\delta}, \tag{4}$$

where $\beta = \frac{2V}{\Delta H_f}(\gamma_{sv} - \gamma_{lv})$, $z = 3$ for HM and LSM and $z = 2$ for LNG. The δ value is positive only for LSM and zero for the other two cases.

It may be noted from eqs (1)–(4) that the melting temperature varies differently for different melting processes (figure 2). Not only different materials, but different facets of the same material also exhibit different melting processes. As a consequence, different variations of the melting temperature are expected which can be realized when the melting temperature of the same material reported by different researchers are compared. For this purpose, we have compared the melting temperature of Sn and shown in figure 3. The data are taken from refs [6,17,18]. It is evident from the comparison that different researchers have observed different variations of melting temperature.

The difference is due to the difference in surface melting. Experimental results [21,100] reveal surface melting before the complete melting and the surface melting temperature decreases with size. The driving force for the surface melting is thought to be a reduction in the total surface energy $\Delta\gamma$ [101,102]:

$$\Delta\gamma^{\{hkl\}} = \gamma_{sv}^{\{hkl\}} - \gamma_{sl}^{\{hkl\}} - \gamma_{lv} \tag{5}$$

γ_s are surface energies of solid–vapour, solid–liquid and liquid–vapour interfaces of the material and the superscript hkl represents the crystal faces. For most cubic

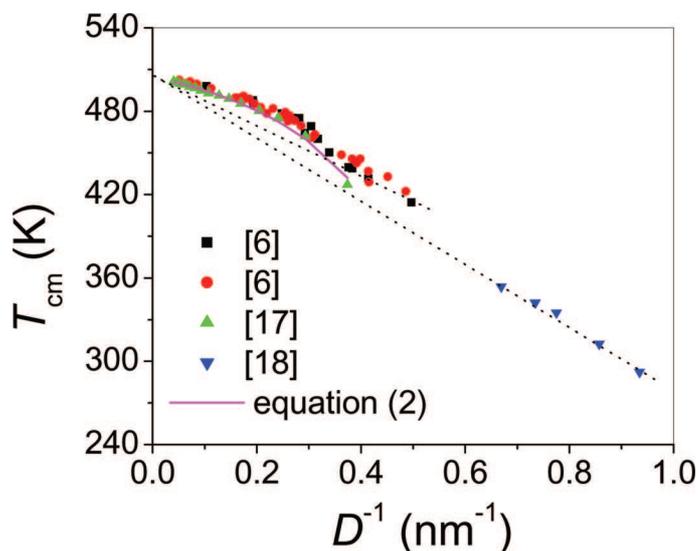


Figure 3. Size-dependent melting of Sn nanoparticles as reported by different researchers.

metals, the ‘average’ driving force for surface melting is close to zero, i.e., $\Delta\gamma \sim 0$, and subtle changes of surface conditions can have marked effects on surface melting as it occurs for $\Delta\gamma > 0$. The orientation dependence of γ_{sv} and γ_{sl} leads to a strong orientation dependence of surface melting [103]. It is known from experiments that the macroscopic Au(110) surface melts at 770 K [104], (100) surface disorders at 970 K [105], while (111) surface is stable up to, and even above, the bulk melting point [106]. Similar melting phenomena have been reported for Au nanoplates [107]. Based on the average value of the surface energies, it can be realized that Ag does not exhibit surface melting [102]. However, MD simulations predict surface melting for Ag(110) surface at a temperature very close to the melting point [108]. Equivalently, T_{SM} of Ag(110) surface is much higher when compared to that of Au(110) though the temperature of complete melting for Ag is lower with respect to Au. The surface melting influences not only the melting but also the evaporation of nanoparticles [109].

3. Melting of non-spherical nanoparticles

Like the case of nanoparticles, similar expressions have also been derived for nanowires and thin films. The ratio between β of nanoparticles and nanowires of infinite length is $\sim 3:2$ for HMM, while the ratio is $\sim 2:1$ for LNG [36]. We are not aware of any report that compares the experimental melting point of nanoparticles and nanowires for the same material. The ratio of slopes evaluated by MD simulations for Pb nanoparticles and nanowires is $\sim 2:1$, while the ratio for Pd is $\sim 3:2$.

Almost all theoretical models assume spherical geometry for nanoparticles. However, supported as well as free nanoparticles are not necessarily spherical. Now, we discuss the melting temperature of nanoparticles with cylindrical geometry. Based on HMM and LNG, the melting temperature of a particle with diameter D and height H , is given by [34,35]

$$T_{\text{cm}} = T_{\text{CM}} \left[1 - \left(\frac{2}{D} + \frac{2}{H} \right) \beta \right] \quad (6a)$$

$$T_{\text{cm}} = T_{\text{CM}} \left[1 - \left(\frac{4}{D} + \frac{2}{H} \right) \beta \right] \quad (6b)$$

respectively. Equation (6) can be applied to cylindrical geometry such as nanowires and nanorods of diameter D and length H . It can also be applied to pancake-like nanoparticles of diameter D and height H .

Dippel *et al* [28] have investigated the size-dependent melting of prism-shaped indium nanoparticles. Recently, we have modified thermodynamic model to understand the size-dependent melting behaviour of the prism-shaped nanoparticles [34]. According to the thermodynamic model, the melting temperature T_{cm} of a prism-shaped nanoparticle is

$$T_{\text{cm}} = T_{\text{CM}} \left[1 - \left(\frac{6.928}{D} + \frac{2}{H} \right) \beta \right], \quad (7)$$

where D is the edge length and H is the height of solid prism-shaped nanoparticles. It may be noted from eq. (7) that melting temperature of an island depends on the size as well as on the height of the prism-shaped nanoparticles.

Analysing the melting temperature of prism-shaped nanoparticles [28], it has been argued that substrate-particle interaction plays a significant role in the melting behaviour of nanoparticles. It has also been shown that the extrapolated bulk melting temperature is lower than the experimental value. The bulk melting temperature cannot be extrapolated from the size-dependent melting curve for $H \neq \infty$. It has also been noted by different researchers that the bulk melting temperature cannot be extrapolated from the nanoscale results [30,34,35,110–113]. MD simulations of Ti nanowires and Ni clusters also predict similar results. The extrapolated bulk melting temperature for nanowires or clusters is lower than the experimental values. In the case of Zn nanowires also, the extrapolated value is lower than the bulk melting temperature [30,35]. We have plotted the melting temperature of prism-shaped indium nanoparticles [34] as a function of the inverse of the size of the islands for different height H and shown in figure 4. It may be noted that the extrapolated bulk melting temperature is closer to the experimental one for large H value. Thus, the extrapolated value will always be lower than the bulk melting temperature as long as H is finite. In some cases, the higher value of bulk melting temperature is realized when extrapolated from the nanoscale results [20–22] and is thought to be due to structural difference [20]. The size-dependent melting temperature of Pb nanoparticles [22] is shown in figure 5. It is clear that the extrapolated bulk melting temperature is higher than the bulk melting temperature of Pb.

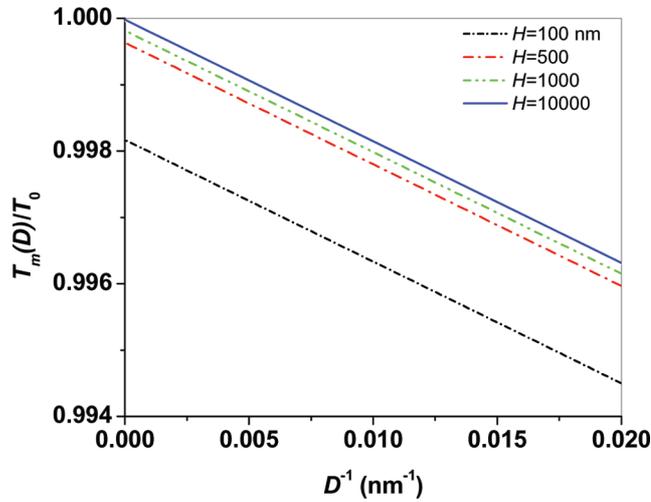


Figure 4. Melting temperature of prism-shaped nanoparticles [34] of edge length D and height H .

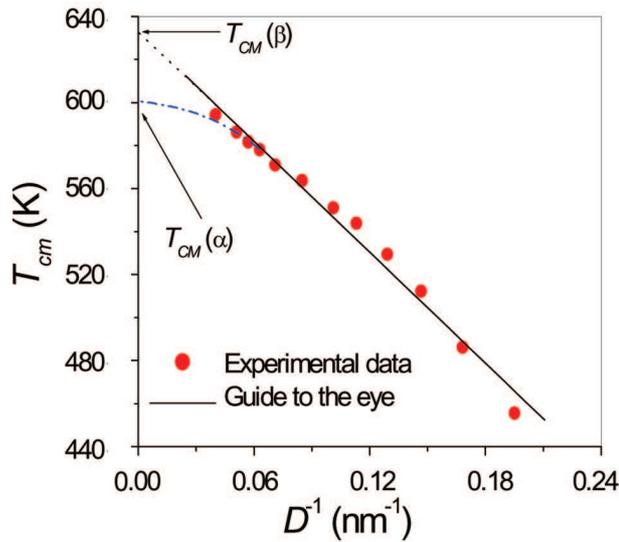


Figure 5. Melting of Pb nanoparticles with two different phases. The data are taken from ref. [22].

4. Melting of supported nanoparticles

Thermodynamic as well as other theoretical models assume spherical shape and yield a linear relationship between the melting temperature and the inverse of the particle size that is in accordance with most of the experimental results. However, nanometer-sized islands deposited on a substrate are generally non-spherical.

It has been argued that the constant of proportionality between the decrease in melting point and the surface curvature does not depend on whether the particle is supported or free. The melting temperature of a supported particle that has a free surface is found to be the same as that of a free spherical particle with the same surface curvature [71]. However, thermodynamic model predicts a difference and the melting temperature is predicted to be dependent on the contact angle [72,73]. In other words, the slope of the variation will be different depending upon the substrate–particle interaction.

5. Superheating of nanoparticles

Embedded nanocrystals occasionally behave differently. Superheating has been reported for nanoparticles embedded in some matrices while the same nanoparticles when embedded in some other matrices, show lower melting temperature. Superheating has been observed for Pb and In nanocrystals embedded in aluminium matrix [78,79]. Experimental results of Sheng *et al* [78,79] reveal that the enhancement or depression of the melting temperature of the embedded nanoparticles depends on the epitaxy between the nanoparticles and the embedding matrix. This is attributed to the suppression of vibrational motion of the surface atoms by the interface epitaxy. The melting starts from the centre and proceeds towards the surface [114] for embedded nanoparticles, while the melting starts from the surface and proceeds towards the centre for free nanoparticles.

Thermodynamic model can be modified to explain the superheating of nanoparticles in embedded condition [77]. It is written as

$$\frac{T_{cm}}{T_{CM}} = 1 - \frac{6(\gamma_{MS} - \gamma_{ML})}{\rho LD}, \quad (8)$$

where γ_{MS} and γ_{ML} are the interfacial free energies of the matrix–solid and the matrix–liquid interface, respectively, ρ is the density of the particle and L is the latent heat of melting per unit mass. The interfacial energy difference can be expressed by the following equation:

$$\gamma_{MS} - \gamma_{ML} = \gamma_{SL} \cos \theta, \quad (9)$$

where θ is the angle of contact developed at the triple point of solid, liquid and matrix phases. It is evident from eqs (8) and (9) that the melting point of the embedded particles will increase if $\theta < 90^\circ$ and the depression of melting will be observed when $\theta > 90^\circ$. A definite epitaxial relationship between the matrix and the particle suppresses the vibrational motion. The epitaxial relationship suggests that γ_{MS} is smaller than γ_{ML} .

Superheating has been reported for Pb in Al, In in Al, Bi in Zn and Ge in SiO₂ [78–81]. The superheating observed for Ge in SiO₂ indicates that the epitaxial relation between the material and the matrix is not the essential criterion of superheating. Superheating has also been reported for free nanoparticles and is thought to be due to the different phases of the materials when reduced to nanodimension. Materials like Sn with 10–30 atoms remain solid at ~50 K above the melting point of bulk tin. This behaviour is possibly related to the fact that the structure of the clusters is completely different from that of the bulk element.

6. Magic melters

Early theoretical and experimental studies of the melting of small particles revealed a melting point depression that scales as approximately $1/D$. This behaviour can be understood from a simple thermodynamic argument using the surface energy and the surface-to-volume ratio. The $1/D$ dependence breaks down for particles with less than around 500 atoms. Irregular variation of melting temperature with cluster size has also been reported. The geometry of nanoparticles decides the melting temperature of the clusters. The observed pattern of maxima and minima in T_{cm} cannot be fully explained by electronic or geometric shell closings.

7. Summary

We have summarized the important results on the hundred years of thermodynamic model and the melting temperature of nanoparticles. It is shown that thermodynamic model with different hypothesis can be applied to understand the variation of melting temperature of very small sizes without modifying the values of the bulk thermodynamic parameters. Different variations of melting temperature are shown to be due to the different melting behaviour of nanoparticles. The model can easily be modified and applied to understand the melting behaviour of different shaped nanoparticles. Overall, thermodynamic model can be used to understand the size-dependent melting of nanoparticles in the intermediate size range.

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