

A Classical Approach for the Melting of a Bare and Encapsulated Nanorod

Himanshu Kumar Pandey*, Nishit Kumar Pandey**

*Principal, Gyanodaya Gurukul, Patna, India

**PGT, Anchi Devi Sarraf Girls Plus Two School, Madhupur, Jharkhand, India

ABSTRACT

Melting point depression and enhancement of nanomaterials have been found to depend on size, dimension and surface properties of the nanomaterials. Ours is a phenomenological model based on classical considerations regarding melting of nanomaterials. The model extensively discusses a nanorod, a bare nanorod and an encapsulated nanorod separately. We have considered a nanorod and using a simple minded approach of cohesive binding energy observed that the melting point of the nanorod gets depressed as the size goes down. Further, to illustrate the phenomena, we have adopted a classical thermodynamic approach which is mainly based on Gibbs energy of a bare and encapsulated (containing matrix) nanorod. We have minimized the Gibbs energy for the two nanosystems separately in different phases and calculated and analyzed the results for the melting point of the nanorod. The results of our models are consistent with both of experimental results and other thermodynamic models. Keywords : Nanomaterials, Encapsulated Nanorod, Thermodynamic

Introduction

This millennium looks forward for the major advances in materials headed by the significant strides in tailoring and characterizing materials on the nanometer scale. The physical properties of nanoparticles are a subject matter of intense contemporary interest. As the size of low-dimensional materials decreases to nanometer size regime, electronic, magnetic, optic, catalytic and thermodynamic properties of the materials are significantly altered from those of either the bulk or a single molecule.[46] Owing to the change of the properties, the fabrication of nanostructural materials and devices with unique properties in atomic scale has become an emerging interdisciplinary field involving solid-state physics, chemistry, biology and materials science. Also, this field of research is of special importance for the study of initial stages of thin film growth in the area of microelectronics. Among the above counted special properties of nanocrystals, the melting point of nanocrystals is one of the important thermodynamic characteristics which determine many properties of materials. Thus a thorough understanding of the thermal properties of low dimensional materials is of importance due to their potential applications in the field of microelectronics, solar energy utilization and nonlinear optical materials also. This may allow the use of a greater variety of substrates or the formation of laminar thin

films without thermal damage to the underlying features. The most striking example of the deviation of the corresponding conventional bulk thermodynamic behavior is probably the depression of the melting point of nanostructures. A relation between the size of nanostructures and melting temperature was first established by Pawlow in 1909 and Takagi in 1954 demonstrated experimentally for the first time that ultrafine metallic particles melt below their corresponding bulk temperatures.[20, 47] Further studies revealed that isolated and substrate-supported nanoparticles with relatively free surfaces usually exhibit a significant decrease in melting temperature as compared to the corresponding conventional bulk materials. The physical origin for this phenomenon is that the ratio of the number of surface to volume atoms is enormous, and the liquid/vapor interface energy is generally lower than the average solid/vapor interface energy.[48] Therefore as the particle size decreases, its surface to volume atom ratio increases and the melting temperature decreases as a consequence of the improved free energy at the particle surface. Moreover, the metallic and organic nanocrystals can exhibit not only a decrease of the melting point, but also a superheating , depending on their surrounding environments. [23,25,27]

It is widely believed that the melting temperature T_m of nanostructures goes down with decreasing size. The theory for this claim is usually based by considering spherical shaped nanostructures. The methodology used ranges from a variety of classical approaches to the first principle quantum mechanical calculations. [1,2]. We shall study a novel nanosystem namely a nanorod. We adopt a classical thermodynamics approach in which we shall minimize the Gibbs energy.

An elementary approach (Weizsaker Model)

Let us first adopt a simple minded approach based on calculating the cohesive energy for a nearest neighbour interacting nanorod. Figure 1 depicts such a nanorod.

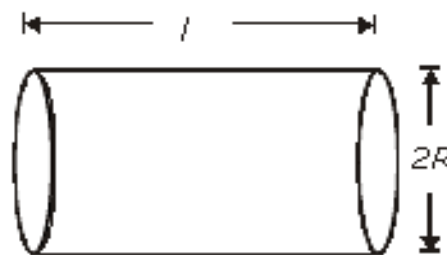


Fig. 1 Schematic nanorod of length l and radius R .

We can write $E_{Tot} = -NJ + 2\pi R\ell\gamma \dots(1)$

Where J represents the energy per bond and g is a surface energy term. Note that we consider only the curved surface area to be significant.

If the total energy per atom be ϵ then we can also write $E_{Tot} = \frac{\pi R^2\ell}{a_0^3} \epsilon \dots(2)$, where a_0 is the interatomic distance.

Note that the volume V is, $V = \pi R^2 \ell$ and Hence, the total number of atoms N is $N = \frac{\pi R^2 \ell}{a_0^3} \dots\dots(3)$,

whereby the total energy per atom can be written as- $\epsilon = \frac{E_{Tot.}}{N} = -J + \frac{2\pi R \ell}{\pi R^2 \ell} \gamma a_0^3$ which implies

$$\epsilon = -J + \frac{2}{R} \gamma a_0^3 \dots\dots(4)$$

It is reasonable to assume that the melting temperature T_m is related to the binding energy per atom. The greater the binding energy the greater the melting point. Hence $T_m \propto -\epsilon$

which implies, $T_m \propto \left[J - \frac{2}{R} \gamma a_0^3 \right] \dots\dots(5)$

The melting temperature T_m is then $T_m = T_0 - \frac{2}{R} \gamma a_0^3 C_1 \dots\dots(6)$, where T_0 is the bulk melting point and C_1 is a constant.

The above expression indicates that if R goes down the second term on the right hand side of eqn (6) increases thereby decreasing the melting temperature T_m . We must note that R scales with l . A similar argument has been advanced by C.F. Von Weizsaker to explain the nature of binding in a nucleus. It goes under the name of the famous Weizsaker semi empirical mass formula.

TABLE 2: Variations in melting point of GaN cylindrical nanoparticles against the size of the particles.

S. no.	R_i (nm)	$1/R_i$ (nm) ⁻¹	T_{GS} (K)			
			$\gamma_B = 0.05$ J/m ²	$\gamma_B = 0.10$ J/m ²	$\gamma_B = 0.15$ J/m ²	$\gamma_B = 0.20$ J/m ²
1	2.23	0.448	941.41	1038.43	1151.56	1245.51
2	3.52	0.284	1057.22	1179.55	1317.61	1446.46
3	4.69	0.213	1280.02	1415.01	1531.21	1631.29
4	5.61	0.178	1433.81	1515.48	1643.95	1750.56
5	6.64	0.151	1553.06	1637.81	1737.91	1838.37
6	8.38	0.118	1634.36	1728.71	1813.45	1923.12
7	10.61	0.094	1694.18	1782.01	1879.41	1982.56
8	12.17	0.082	1725.63	1810.98	1916.99	2017.07
9	14.29	0.071	1753.62	1844.89	1957.64	2045.45
10	18.19	0.055	1791.21	1879.41	1989.08	2073.83

Gibbs energy based analysis of a bare nanorod

Figure 2 depicts a thin nanorod with R its radius of cross section and ℓ the length ($R \ll \ell$). Melting of the rod is considered only on the curved surface. The surface properties especially the surface energies in various phases play significantly besides others when the study of melting of a nanorod is undertaken. Surface energy quantifies the disruption of intermolecular bonds that occurs when a surface is created. In the physics of solids, surface must be intrinsically less energetically favorable than the bulk of a material; otherwise there would be a driving force for surfaces to be created and surface is all there would be. The surface energy may therefore be defined as the excess energy at the surface of a material compared to the bulk. We can start with equating the mass of the melted cylindrical shell in the solid and liquid phases as-

Table-I; Describes the various quantities used in the analysis

Table-I

<i>Symbol</i>	<i>Meaning</i>
ρ_s	Density of the solid phase of the nanorod
ρ_ℓ	Density of the liquid phase of the nanorod
σ_s	Surface thickness of the outer melted shell of the nanorod.
$(R - \sigma_s)$	Radius of the solid phase of the nanorod which does not melt
a	ρ_s / ρ_ℓ
B	σ_s / R
R_ℓ	Radius of the liquid state of the nanorod
$\gamma_{\ell m}$	Surface energy of the liquid matrix-interface of the nanorod
$\gamma_{s\ell}$	Surface energy of the solid liquid-interface of the nanorod
γ_{sv}	Surface energy of the solid-vapor interface of the nanorod

Symbols used in the analysis in this chapter.

Mass of the melted shell in solid phase = mass of the melted shell in liquid phase.

i.e.

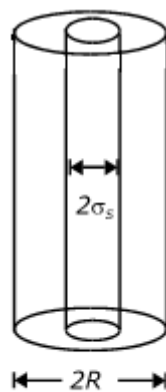


fig. 2

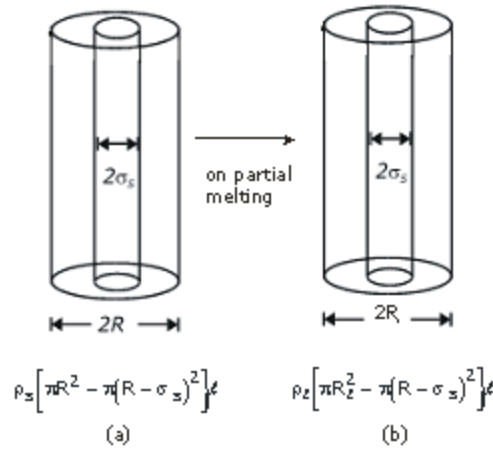


fig. 3

(The symbols used in the analysis are explained in Table I)

$$\text{i.e. } \pi \rho_s [R^2 - (R - \sigma_s)^2] \ell = \pi \rho_l [R_l^2 - (R - \sigma_s)^2] \ell$$

Here our aim is to define R_l in terms of σ_s . Therefore, $R_l^2 = \alpha R^2 - (R - \sigma_s)^2 (\alpha - 1) \dots (7)$

$$\text{which implies } R_l^2 = R^2 [\alpha - (\alpha - 1)(1 - B)^2] \dots (8)$$

$$\text{Thereby } R_l^2 = R^2 [1 - (\alpha - 1)B(B - 2)] \dots (9)$$

$$\text{We consider the ratio } \frac{R_l^2}{R^2} = [1 - (\alpha - 1)B(B - 2)] \dots (10)$$

$$\text{Whereby we can further write } \frac{R_l}{R} = [1 - (\alpha - 1)B(B - 2)]^{1/2} \dots (11)$$

$$\text{Taylor expanding the R.H.S of eqn.(11), we obtain } \frac{R_l}{R} \approx 1 - \frac{(\alpha - 1)B(B - 2)}{2} - \frac{1}{8}(\alpha - 1)^2 B^2 (B - 2)^2$$

Rearranging we get to order B^2 (i.e. ignoring terms of order B^3 and higher)

$$\frac{R_l}{R} \approx 1 + \frac{(\alpha - 1)}{2} 2B + (\alpha - 1) \left[\frac{-B^2}{2} - \frac{(\alpha - 1)}{8} 4B^2 \right]$$

$$\text{which implies } \frac{R_l}{R} \approx 1 + B(\alpha - 1) + \frac{\alpha - 1}{2} B^2 (-1 - \alpha + 1)$$

$$\text{Simplifying we have } \frac{R_l}{R} \approx 1 + B(\alpha - 1) + \frac{\alpha - 1}{2} B^2 \alpha \dots (12)$$

$$\text{We thus have } \frac{R_l}{R} \approx R [1 + B(\alpha - 1) + \frac{\alpha - 1}{2} B^2 \alpha] \dots (13)$$

We now differentiate the above expression to obtain $\frac{R_l}{R} \approx R \left[\frac{(\alpha - 1)}{R} + \left(\frac{\alpha - 1}{2} \right) \frac{2B}{R} \alpha \right]$ (note that

$$B = \frac{\sigma_s}{R} \text{ and hence } \frac{dB}{d\sigma_s} = \frac{1}{R})$$

$$\text{Therefore } \frac{dR_l}{d\sigma_s} \approx (\alpha - 1)[1 - \alpha \beta] \dots (14)$$

$$\text{We already have from eqn. (10) } \frac{R_l^2}{R^2} = [1 - (\alpha - 1)B(B - 2)]$$

Differentiating once again the above expression We have

$$\frac{d(R_\ell^2)}{d6_s} = R^2 \left[-(\alpha - 1) \left(\frac{2B}{R} - \frac{2}{R} \right) \right] \text{ i.e } \frac{d(R_\ell^2)}{d6_s} = 2R [(\alpha - 1)(1 - B)] \dots (15)$$

The central part of this analysis is to equate Gibbs energy in various phases.

Note that the Gibbs energy is $G = (U + PV - TS)_s + (U + PV - TS)_\ell + 2\pi\ell\gamma_{s\ell}(R - \sigma_s)$

$$+ 2\pi \left[\gamma_{\ell v} \{ R_\ell^2 - (R - \sigma_s)^2 \} + \gamma_{sv} (R - \sigma_s)^2 \right] \dots (16), \text{ where the symbols have their usual meanings. We}$$

minimize the Gibbs energy with respect to σ_s which gives

$$\frac{dG}{d\sigma_s} = 0 \dots (17)$$

One can break-up the Gibbs energy into three components $G = G_1 + G_2 + G_3 \dots (18)$

With $G_1 = (U + PV - TS)_s + (U + PV - TS)_\ell$ whereby

$G_1 = m(T_m - T_0)\Delta S = \pi(R - \sigma_s)^2 \ell \rho_s (T_m - T_0)\Delta S$, where m is the mass of nanorod in the solid and liquid phases.

So $G_1 = \pi R^2 (1 - B)^2 \ell \rho_s (T_m - T_0)\Delta S = \pi R^2 (1 - B)^2 \ell \rho_s (T_m - T_0)L$, where L is latent heat. (19)

$$G_2 = 2\pi\ell\gamma_{s\ell}(R - \sigma_s) \dots (20) \text{ And } G_3 = 2\pi \left[\gamma_{\ell v} \{ R_\ell^2 - (R - \sigma_s)^2 \} + \gamma_{sv} (R - \sigma_s)^2 \right] \dots (21)$$

We extremise these components G_1, G_2 and G_3 with respect to σ_s

$$\frac{dG_1}{d\sigma_s} = L \left(1 - \frac{T_m}{T_0} \right) \rho_s 2\pi R \ell (1 - B) \quad \left[\because B = \frac{\sigma_s}{R}; \because \frac{dB}{d\sigma_s} = \frac{1}{R} \right] \dots (22)$$

$$\frac{dG_2}{d\sigma_s} = -2\pi\ell\gamma_{s\ell} \dots (23)$$

$$\frac{dG_3}{d\sigma_s} = 4\pi R (1 - B) [\gamma_{\ell v} (\alpha - 1) + \gamma_{\ell v} - \gamma_{sv}] \dots (24)$$

$$\frac{dG_3}{d\sigma_s} = 4\pi R (1 - B) [\alpha\gamma_{\ell v} - \gamma_{sv}] \dots (25)$$

where we have used eqn. (13)

We can also write $\frac{d}{d\sigma_s} (1 - B)^2 = -2 \frac{(1 - B)}{R} \dots (26)$

Using eqn. (22), (23) and (24), we obtain

$$\frac{dG}{d\sigma_s} = \frac{dG_1}{d\sigma_s} + \frac{dG_2}{d\sigma_s} + \frac{dG_3}{d\sigma_s} = 0 \dots (27)$$

which implies $L \left(1 - \frac{T_m}{T_0} \right) 2\pi\rho_s R (1 - B) \ell - 2\pi\ell\gamma_{s\ell} + 4\pi R (1 - B) [\gamma_{\ell v} (\alpha - 1) + \gamma_{\ell v} - \gamma_{sv}] = 0 \dots (28)$

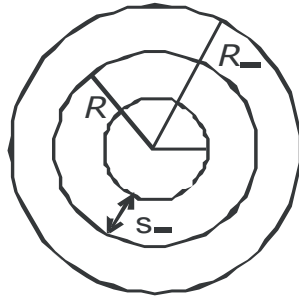


Fig. 4 Before melting.

This lengthy exercise finally is
$$\frac{T_m}{T_0} = 1 - \frac{1}{R\rho_s L} \left[\frac{\gamma_{sl}}{(1-B)} - \frac{2R}{\ell} (\gamma_{lv}\alpha - \gamma_{sv}) \right] \dots(29)$$

We can now analyze the above expression for the melting point as

- (i) If R and/or L be large, the denominator of the coefficient of the second term on the right hand side of eqn.(29) goes smaller and can be approximated to zero which provides $T_m \approx T_0$

If the density of the solid nanorod is large, T_m is approximately closer to the bulk temperature T_0 . The undetermined parameter is s_m i.e., the melted thickness. Thus it may be reasonable to define melting when s_m/R is equal to 0.1.

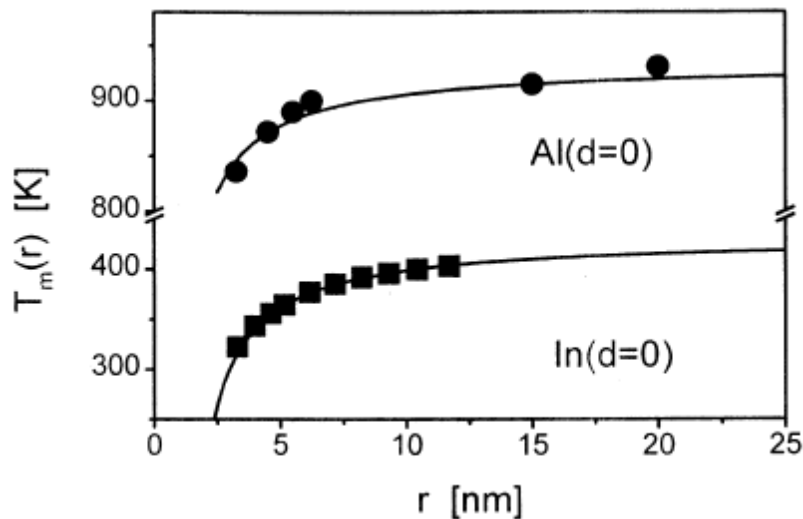


Fig. (5) T_m as function of Al and In nanoparticles the solid lines are theoretical predictions. Symbols (l) denote the experimental results of T_m values of Al nanoparticles. Symbols (n) denote the experimental results of T_m values of In nanoparticles.

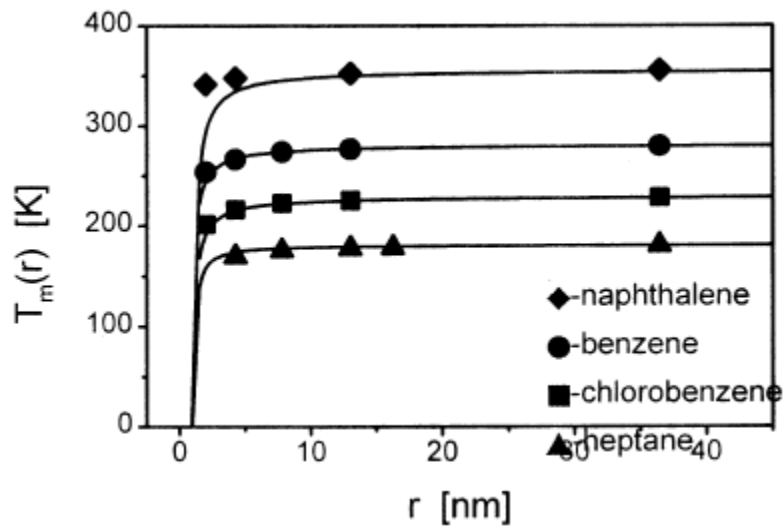


Fig.(6) T_m functions of four organic nanorods: Benzene, Chlorobenzene, heptane and naphthalene. The solid lines of theoretical predictions and the symbols \diamond , \bullet , \blacksquare , \blacktriangle denote the experimental results of Benzene, Chlorobenzene, heptane and naphthalene respectively.

In general, We have $T_m = T_0 - \frac{\beta}{R}$, Where $\beta = \frac{1}{\rho_s \ell}$, the coefficient of the 2nd term of the R.H.S. of eqn.

(29).

Therefore, we observe that as the size R goes down, T_m goes down. We also note that the coefficient β depends inversely on the latent heat L. Clearly, as the latent heat L decreases, T_m decreases. If β is positive, we obtain the T_m vs $1/R$ plot as shown in fig.-5, which clearly indicates that T_m decreases as $1/R$ increases.

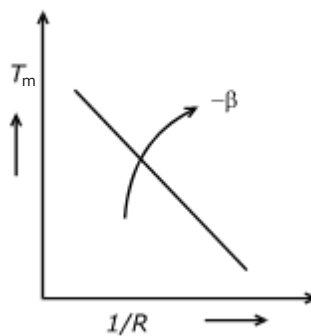


Fig. 5

(iii) When β is negative, superheating may arise. Considering the three terms within the box of the second, term on the right hand side of eqn. (29), the possibility of superheating can be analyzed.

Superheating is possible only if $\alpha\gamma_{lv} > \gamma_{sv}$, because the last term is small on account of being dependent on $\frac{R}{\ell}$

(iv) We can readily proceed with writing $T_m = f^n\left(\frac{\sigma_s}{R}\right)$; $\frac{\sigma_s}{R} = 0.1$

Dependence of $\frac{\sigma_s}{R}$ is studied for a typical system like indium (In) with $\frac{\sigma_s}{R}$ ranging from 0.05 to 0.2 in the steps of 0.05. The results were in a good agreement as expected theoretically.

(IV) **Gibbs energy based analysis of an encapsulated nanorod**

We consider an encapsulated nanorod with its radius of cross section as R , the radius of the surrounding matrix shell being R_m and $(R-s_s)$, the radius of its inner shell. Fig. 6 depicts such a nanorod and figs. 7(a) and 7(b) show the cross sectional view of the nanorod before and after melting. R_m and R are the radii of the nanorod upto the matrix and the solid portion respectively. $(R-s_s)$ represents the portion of the nanorod which does not melt on heating.

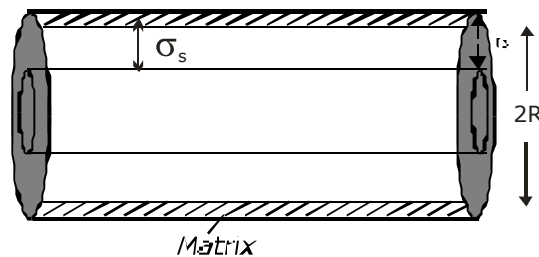


Fig. 6 Encapsulated nanorod



Fig. 7(a) cross-sectional view of the nanorod before melting of shell Fig. 7(b) cross-sectional view of the cylinder on melting of shell

We can proceed with the statement of Gibbs energy for the system as:

$$G = (U + PV - TS)_s + (U + PV - TS)_\ell + 2\pi\ell [R_\ell\gamma_{\ell m} + \gamma_{s\ell}(R - \sigma_s) + R_m\gamma_{mv}] + 2\pi \left[\gamma_{lv} \left\{ R_\ell^2 - (R - \sigma_s)^2 \right\} + \gamma_{sv} (R - \sigma_s)^2 + \gamma_{mv} (R_m^2 - R_\ell^2) \right] \quad \dots(30)$$

As discussed earlier

$$(U + PV - TS)_s + (U + PV - TS)_\ell = L \left(\frac{T_m}{T_0} - 1 \right) \rho_s \pi (1 - B)^2 R^2 \ell \quad \dots(31)$$

Equating the mass of matrix before and after melting $m_m = \pi \ell \rho_m (R_m^2 - R_\ell^2)$

Which yields $R_m^2 = \frac{m_m}{\pi \ell \rho_m} + R_\ell^2 \dots (32)$

We consider an imaginary rod of radius R_0 consisting of the matrix material $m_m = \pi R_0^2 \ell \rho_m$

Thus $R_m^2 = R_0^2 + R_\ell^2$, which implies, $R_m^2 = R_0^2 + R_\ell^2 \left[1 + (\alpha - 1) \frac{\sigma_s}{R} \left(2 - \frac{\sigma_s}{R} \right) \right] \dots (33)$

We consider two cases

(i) For a thin shell we consider the following first order adjustment with

$$R_m \approx R_l \Rightarrow \frac{dR_m}{d\sigma_s} = \frac{dR_l}{d\sigma_s}$$

Where, $R_m = \left[R_\ell^2 \left(1 + \frac{R_0^2}{R_\ell^2} \right) \right]^{1/2} = R_\ell \left(1 + \frac{1}{2} \frac{R_0^2}{R_\ell^2} \right) \dots (35)$

For thin shell, eqn (30) can be re-written as

$$G = L \left(\frac{T_m}{T_0} - 1 \right) \rho_s \pi (1 - B)^2 R^2 \ell + 2\pi \ell \left[R_\ell \gamma_{\ell m} + \gamma_{s\ell} (R - \sigma_s) + \gamma_{mv} R_\ell \right] + 2\pi \left[\gamma_{\ell v} \left\{ R_\ell^2 - (R - \sigma_s)^2 \right\} + \gamma_{sv} (R - \sigma_s)^2 \right] \dots (36)$$

Because for thin shell $R_m \approx R_l \dots (37)$

Extremising Gibbs energy with respect to σ_s we find $\frac{dG}{d\sigma_s} = 0 \dots (38)$

This implies

$$L \left(\frac{T_m}{T_0} - 1 \right) 2\pi \rho_s R (1 - B) \ell + 2\pi \ell \gamma_{\ell m} (\alpha - 1) (1 - \alpha B) - 2\pi \ell \gamma_{s\ell} + 2\pi \ell \gamma_{mv} (\alpha - 1) (1 - \alpha B) + 4\pi R (1 - B) \left[\gamma_{\ell v} (\alpha - 1) + \gamma_{\ell v} - \gamma_{sv} \right] = 0 \dots (39)$$

This gives

$$\frac{T_m}{T_0} = 1 - \frac{1}{R \rho_s L} \left[\frac{\gamma_{s\ell} - \gamma_{\ell m} (\alpha - 1) (1 - \alpha B)}{(1 - B)} - \frac{\gamma_{mv} (\alpha - 1) (1 - \alpha B)}{(1 - B)} - \frac{2R}{\ell} (\gamma_{\ell v} \alpha - \gamma_{sv}) \right] \dots (40)$$

This ultimately reduces to

$$\frac{T_m}{T_0} = 1 - \frac{1}{R \rho_s L} \left[\frac{\gamma_{s\ell} - (\alpha - 1) (1 - \alpha B) (\gamma_{\ell m} + \gamma_{mv})}{(1 - B)} - \frac{2R}{\ell} (\alpha \gamma_{\ell v} - \gamma_{sv}) \right] \dots (41)$$

(ii) For thick shell $R_m > R_l$, Therefore, $\gamma_{mv} (R_m^2 - R_l^2) = \gamma_{mv} R_0^2 \dots(42)$

But $R_0^2 = R_m^2 - R_l^2$, which gives $R_0 = (R_m^2 - R_l^2)^{1/2}$

$$\text{Therefore, } \frac{dR_0}{d\sigma_s} = \frac{-R_l(\alpha-1)(1-\alpha B)}{(R_m^2 - R_l^2)^{1/2}} = -\frac{R_l}{R_0}(\alpha-1)(1-\alpha B) \dots(43)$$

we must note that the matrix in general takes relatively larger time to melt therefore we can consider

$$R_m \text{ to be independent of } \sigma_s \text{ i.e., } \frac{dR_m}{d\sigma_s} = 0 \text{ And } \frac{dR_0^2}{d\sigma_s} = -2R(\alpha-1)(1-B) \dots(44)$$

The Gibbs energy for the thick shell of the nanorod can be written as

$$G = L \left(\frac{T_m}{T_0} - 1 \right) \rho_s \pi (1-B)^2 R^2 \ell + 2\pi \ell \left[\gamma_{sl} (R - \sigma_s) + R_l \gamma_{lm} + R_0 \gamma_{mv} \right] + 2\pi \left[\gamma_{lv} \left\{ R_l^2 - (R - \sigma_s)^2 \right\} + \gamma_{sv} (R - \sigma_s)^2 + \gamma_{mv} (R_0^2 - R_l^2) \right] \dots(45)$$

Extremizing the Gibbs energy with respect to σ_s we obtain $\frac{dG}{d\sigma_s} = 0$

$$\text{Which gives } \frac{T_m}{T_0} = 1 - \frac{1}{R \rho_s L} \left[\left\{ \gamma_{sl} - (\alpha-1)(1-\alpha B) \left(\gamma_{lm} - \frac{R_l}{R_0} \gamma_{mv} \right) \right\} \frac{1}{(1-B)} - \frac{2R}{\ell} \left\{ \alpha \gamma_{lv} + \gamma_{sv} - 2\gamma_{mv} (\alpha-1) \right\} \right] \dots(46)$$

Results and Discussion

We can now summarize the above discussion for the melting point of the bare and encapsulated nanorod. At nanoscales, particles exhibit many thermophysical features distinct from those found at microscales. As the size decreases due to the increase in surface to volume ratio the melting temperature deviates from the bulk values and becomes a size-dependent property. This change in melting point is primarily caused besides others because nanoscale materials have a much larger surface surface to volume ratio than bulk materials, drastically altering their thermodynamic and thermal properties. This decrease may be of the order of the order of tens to hundreds of degrees for metals for with nanometer dimensions. Surface atoms bind in the solid phase with less cohesive energy because they have fewer neighboring atoms in close proximity compared to atoms in the bulk of the solid. It is well established that the melting

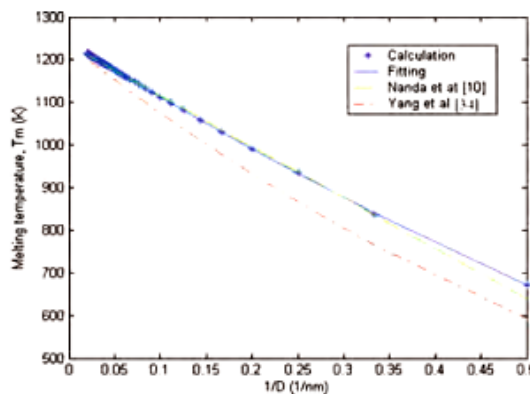


Fig. 8. Melting point vs the reciprocal of nanoparticle diameter. The solid line is the fitting result. The dashed line is the result calculated from the thermodynamic model

temperature of Au(1064K) decreases when the particle dimensions are reduced to the nanoscale. Therefore, at 3 nm diameter, Au particles can melt at temperature ~ 500 K. Similarly, the melting temperature of B₄C (2450K) lowered to ~ 764 K range with spherical-shaped and ~ 495 K ranges with cylindrical nanorods. Also, GaN (2770 K) nanorods are observed to melt at the temperature ~ 1553 K range.

As an elementary approach we observe through eqn.(6) that if R goes down the second term on the right hand side of eqn (6) increases thereby decreasing the melting temperature T_m . We must note that R scales with l . A similar argument has also been advanced by C.F. Von Weizsacker to explain the nature of binding in a nucleus. It goes under the name of the famous Weizsacker semi empirical mass formula.

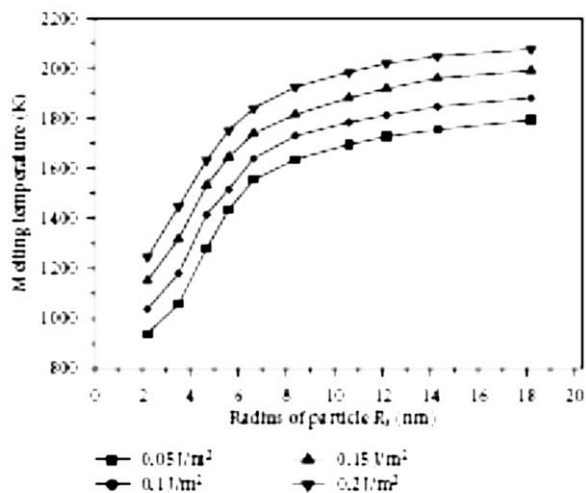


Figure 3: Variation of melting point of GaN cylindrical nanoparticles against the size of the particles.

The expressions for the melting point of the bare and encapsulated nanorod as discussed by eqns. (29), (41) and (46) suggest us that

- (i) If the size of the nanorod R and / or L be large, the denominator of the coefficient of the second term on the right hand side of eqns. (29), (41) and (46) goes smaller and can be approximated to zero which provides $T_m \approx T_0$

If the density of the solid nanorod is larger then T_m is once again closer to the bulk temperature T_0 . The undetermined parameter is s_s i.e., the melted thickness.

In general, We have, $T_m = T_0 - \frac{\beta}{R}$, Where $\beta = \frac{1}{\rho_s \ell}$,

Therefore, we observe that as the size R goes down, T_m goes down. We also note that the coefficient β depends inversely on the latent heat L. Clearly, as the latent heat L decreases, T_m decreases. If β is positive, we obtain the T_m vs $1/R$ plot as shown in fig.-8, which clearly indicates that T_m decreases as $1/R$ increases.

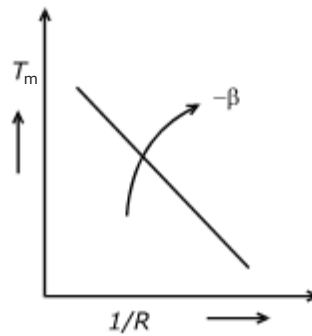


Fig. 8

(iii) We have assumed that b is positive. However, the possibility of b being negative cannot be ruled out. This would imply a superheating. Considering the three terms within the box of the second term on the right hand side of eqn. (41) (note $b < 1$), the possibility of superheating can arise.

Superheating is possible if $\alpha\gamma_{lv} < \gamma_{sv}$ and $\gamma_{lm} + \gamma_{mv} > \gamma_{sl}$

It should be noted that when the surface atoms of the particles is smaller than that of the interior atoms due to the coherent interfaces between the particles and the matrix, the superheating of the nanorod is evident. T_m decreases as r decreases.

Clearly it is observed that the melting temperature decreases when the particle size reduces.

References

- [1]. V.K. Semenchenko, Surface Phenomna in Metals and Allys (Pergamon, Oxford, United Kingdom, 1961)p,281.
- [2]. J.R. Sambles, Proc. R. Soc. A 324, 339 (1971).
- [3]. Ph. Buffat and J.P. Borel, Phys. Rev. A 13, 2287 (1976).
- [4]. P.R. Couchman and W.A. Jesser, Nature 269, 481 (1977).
- [5]. G.L. Allen, W.W. Gile, and W.A. Jesser, Acta, Metall. 28, 1695 (1980).
- [6]. V.P. Skripov, V.P. Koverda, and V.N. Skokov, Phys. Status Solidi A 66, 109 (1981).
- [7]. T.Castro, R. Reifenberger, E.Choi, and R.P. Andres, Phys. Rev. B 42, 8548 (1990).
- [8]. A.N. Goldstein, C.M. Echer, and A.P. Alivistos, Science 256, 1425 (1992).
- [9]. J.Eckert, J.C. Holzer, C.C. Ahn, Z., Fu, and W.L. Johnson, Nanostruct. Mater, 2, 407 (1993).
- [10]. F.G. Shi, J. Mater, Rees. 9, 1307 (1994).
- [11]. T.Ben David, Y. Lereah, G. Deutscher, R. Kofmans, and P. Cheyssac, Philos, Mag. A 71, 1135 (1995)
- [12]. S.L. Lai, J.Y. Guo, V. Petrova, G. Ramanath, and L.H. Allen, Phys, Rev. Lett 77, 99 (1996).
- [13]. G.P. Johari, Philos, Mag. A 71, 1135 (1995).
- [14]. K.F. Peters, J.B. Cohen, and Y-W. Chung, Phys. Rev. B 57, 13430 (1998).
- [15]. K. Morishige and K. Kawano, J. Phys. Chem. B 103, 7906 (1999).
- [16]. Q. Jiang, H.X. Shi, and M. Zhao, J. Chem. Phys. 33, 2653 (2000).
- [17]. Z. Zhang, J.C. Li, and Q. Jiang, HJ. Phys. D: Appl. Phys. 33, 2653 (2000).
- [18]. Z. Wen, M. Zhao, and Q. Jiang, J. Phys. Condens. Mater. 12, 8819 (2000).
- [19]. Z. Zhang, . Zhao, and Q. Jiang, Semicond. Sci. Technol. 16, L33 (2001)
- [20]. P. Pawlow, Z. Phys. Chem. 65, 545 (1909).

- [21]. K.J. Hanszen, Z. Phys. 157, 523 (1960).
- [22]. D.R.H., Jones. J.Mater. Sci. 9, 1 (1974).
- [23]. H.Saka, Y. Nishikawa, and T. Imura, Phil. Mag. A 57, 895 (1988).
- [24]. L. Graback and J. Bohr, Phys. Rev. Lett. 64, 934 (1990).
- [25]. D.L. Zhang and B. Cantor, Acta Metall. Mater. 39, 1595 (1991).
- [26]. R Goswami and K. Chattopadhyay, Philos. Mag. Lett. 68, 215 (1993)/
- [27]. H.W. Sheng. G. Ren. L.M. Peng. Z.Q. Hu, and K.Lu, Philos. Mag. Lett. 73, 179 (1996).
- [28]. K.Lu, H.W. Sheng, and Z.H. Jin, Chinese J. Mater, Res. 11, 658 (1997, in Chiense)
- [29]. H.W. Sheng, G. Ren, L.M. Peng, Z.Q. Hu, and K. Lu, J. Mater. Res. 12, 119 (1997).
- [30]. K. Chatoopadhyay and R. Goswami, Prog. Mater. Sci. 42, 287 (1997).
- [31]. L. Zhang, Z.H. Jin, L.H. Zhang, M.L. Sui, and K. Lu, Phys. Rev. Lett. 85, 1484 (2000).
- [32]. Q. Jiang, Z. Zhang, and J.C. Li, Chem. Phys. Lett 322, 549 (2000).
- [33]. Q. Jinag, Z. Zhang, and J.C. Li, Acta Mater, 48, 4791 (2000).
- [34]. Q. Jiang, L.H. Liang, and J.C. Li, J. Phys. Condens Mater 13, 565 (2001).
- [35]. H. Reiss and L.B. Wilson, J. Colloid Scin, 3, 551, (1948).
- [36]. Q. Jiang, H.x. Shi and M. Zhao, acta Meter, 47, 2109 (1999).
- [37]. F.A. Lindemann, Z. Phys.11, 609 (1910).
- [38]. N.F. Mott, Proc. R. Soc. A 146, 465 (1934).
- [39]. A.R. Regel and V.M. Glazov, Semiconductors 29, 405 (1995).
- [40]. H.K. King. In Physical Metallurgy, edited by R.W. Cahn (North Holland, Amsterdam, The Netherland 1970), pp 59-63.
- [41]. Table of Periodic Properties of the Elements (Sargent Welch Scientific, Skokie, IL 1980), p. 1.
- [42]. A.R. Ubbelohde, Melting and Crystal Structure (Clarendon Press, Oxford, United Kingdom, 1965), p.171.
- [43]. J.W.M. Frenken and J.F. van der Veen, Phys. Rev. Lett. 54, 134 (1985).
- [44]. E.T. Chen, R.N. Barenett, and U. Landman, Phys. Rev. B 41, 439 (1990).
- [45]. Antonelli, S.N. Khanna, and P. Jena, Phys. Rev. B 48, 8263 (1993).
- [46]. 46.H.Gleiter,Acta Mater.2000,48,1.
- [47]. M.Takagi, J Phys. Soc. Jpn. 1954, 9, 359
- [48]. O. Gulseren, F. Ercolessi, E. Tossati, Phys Rev. 1995, B51, 7377.