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Abstract
A model has been developed to account for the dependence of melting temperature on the size of nanosolids (nanoparticles, nanowires and nanofilms). In this model the effect of particle size and shape, lattice and surface packing factor, and the coordination number of the lattice and of the surface crystalline planes are considered. A general equation is proposed, having nonlinear form as a function of the reciprocal of nanosolid size. This model is consistent with reported experimental data for nanoparticles of In and Au, nanowires of Pb and In, and nanofilms of In.

1. Introduction

It has been reported that when the size of a solid particle reduces to the nanometre scale, the surface-to-volume ratio is increased and the melting temperature remarkably decreased [1–5]. Thermodynamical properties of nanosolids (nanoparticles, nanowires and nanofilms) are different from those of bulk material, and are dependent on size [6–9]. For design of new materials, it is essential to understand these new thermodynamical properties [10, 11], and several models have been developed to explain the dependence of melting temperature on the size of the nanosolids [12–22]. In most of these models the melting temperature is a linear function of the reciprocal size [12, 15, 17, 20–23].

In this paper we discuss the effect of size on the melting temperature of nanosolids by considering the ratio of the number of surface atoms to the total number of atoms, taking into account the effect of lattice and surface packing factors, and the coordination number of the lattice and surface crystalline planes. We compare the present model with the work of Qi [22], the liquid drop model [20], and available experimental data.

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2. The model

The melting temperature of a solid is proportional to its cohesive energy [23], i.e. proportional to the total bond energy. For a nanosolid this can be written as

$$E_{cn} = (\tfrac{1}{2}n_i\beta_L + \tfrac{1}{2}n_s\beta_S)\varepsilon = \tfrac{1}{2}(n_t\beta_L - (\beta_L - \beta_S)n_s)\varepsilon \qquad (1)$$

where E_{cn} is the cohesive energy of the nanosolid, ε is the energy of each bond, n_i and n_s are the numbers of interior and surface atoms, respectively, and n_t is the total number of atoms in the nanosolid. The parameters β_L and β_S are the coordination numbers of atoms in the lattice and the surface crystalline planes, respectively. Note that β_S is the number of surface bonds, without considering bonds to interior atoms. The cohesive energy, E_0 for bulk material with n_t atoms, is

$$E_0 = \tfrac{1}{2}n_t\beta_L\varepsilon. \qquad (2)$$

Since the melting temperature is proportional to cohesive energy, we have

$$\frac{T_{mn}}{T_{mb}} = \frac{E_{cn}}{E_0} = \frac{n_t\beta_L - (\beta_L - \beta_S)n_S}{n_t\beta_L} = 1 - \frac{(\beta_L - \beta_S)}{\beta_L}\frac{n_S}{n_t} \qquad (3)$$

where T_{mn} and T_{mb} are the melting temperature of nanosolid and bulk material, respectively. If we define a parameter, q, as the surface-to-volume coordination number ratio, $q = \beta_S/\beta_L$, we can write equation (3) as

$$\frac{T_{mn}}{T_{mb}} = 1 - (1-q)\frac{n_s}{n_t}. \qquad (4)$$

Equation (4) can be considered as a general equation for all nanosolids (nanoparticles, nanowires, nanofilms) and, for each of these, it is only required to calculate the n_s/n_t ratio.

2.1. Nanoparticles

To calculate n_s/n_t for all shapes of nanoparticles we define a shape factor, α, as

$$\alpha = \frac{S'}{S} \qquad (5)$$

where S and S' are the surface areas of spherical and non-spherical nanoparticles with equal volume, respectively. Hence, $S' = \alpha S = 4\alpha\pi R^2$, where R is the radius of a spherical nanoparticle with the same volume as the non-spherical particle being considered.

We introduce a parameter, P_S, which represents the packing fraction on a surface crystalline plane (the ratio of the plane area occupied by atoms to the total plane area). For example, for the (111) close-packed plane of a face-centred cubic (fcc) structure, the area 'covered' by an atom of radius, r, is equal to its cross-section (πr^2), and the total surface area associated with each atom is $2\sqrt{3}r^2$. Therefore $P_{S(111),fcc} = \pi r^2/(2\sqrt{3}r^2) = 0.907$. So we can calculate n_s as follows:

$$n_s = P_S\frac{S'}{\pi r^2} = P_S\frac{4\alpha\pi R^2}{\pi r^2} = 4\alpha P_S\frac{R^2}{r^2} \qquad (6)$$

where r is the atomic radius deduced from the atomic volume ($V_a = 4\pi r^3/3$).

We next introduce a lattice packing fraction, P_L, which represents the ratio of the volume of crystal occupied by atoms to the total volume. Using the example of a fcc lattice, the volume of a single atom is $4\pi r^3/3$, and the total volume associated with each atom in the unit cell is $4\sqrt{2}r^3$, so $P_{L,fcc} = (4\pi r^3/3)/(4\sqrt{2}r^3) = 0.740$. For the other standard crystal structures such as the sc (simple cubic), bcc (body-centred cubic), and hcp (hexagonal close packed) the lattice

packing factor (P_L) and the crystalline plane packing factor (P_S) can be calculated in the same way.

To calculate the total number of atoms in the nanoparticle, we must define the outer surface, which is composed of many crystalline planes. A surface crystalline plane is defined as the plane which divides the surface atoms into two equal parts. Therefore the volume of nanoparticle which is occupied with atoms can be calculated as

$$n_i V_a + \tfrac{1}{2} n_s V_a = P_L V_p \tag{7}$$

where V_a is the atomic volume, and V_p is the volume of the particle.

If we divide equation (7) by V_a we have

$$n_i + \tfrac{1}{2} n_s = P_L \frac{V_p}{V_a}. \tag{8}$$

This gives $n_i + n_s/2 = P_L \frac{4\pi R^3/3}{4\pi r^3/3}$, and by considering $n_t = n_i + n_s$, from equations (6) and (8), and after simplifying,

$$n_t = P_L \frac{R^3}{r^3} + 2\alpha P_S \frac{R^2}{r^2}. \tag{9}$$

Therefore, from equations (4), (6), (9),

$$\frac{T_{mp}}{T_{mb}} = 1 - (1-q) \frac{4\alpha P_S \frac{r}{R}}{P_L + 2\alpha P_S \frac{r}{R}} \tag{10}$$

and, by substituting $a = 2\alpha P_S d$, $b = P_L$, $X = 1/D$, where d ($d = 2r$) is the atomic diameter and D ($D = 2R$) is the diameter of the nanoparticle, we can write equation (10) as

$$\frac{T_{mp}}{T_{mb}} = 1 - 2(1-q) \frac{aX}{b + aX}. \tag{11}$$

2.2. Disc-like nanosolids

To calculate the n_s/n_t ratio for a disc-like nanosolid (nanodisc), we assume that D is the diameter and H is the height of the nanodisc. If we replace V_p with V_d in equation (8), we can use this equation to calculate the total number of atoms of a nanodisc, i.e. $n_i V_a + n_s V_a/2 = P_L V_d$, where $V_d = \pi D^2 H/4$ is the volume of the nanodisc. Therefore we can write

$$n_i + \tfrac{1}{2} n_s = P_L \frac{\pi D^2 H/4}{\pi d^3/6} = \tfrac{3}{2} P_L H \frac{D^2}{d^3}. \tag{12}$$

And also, for n_s,

$$n_s = P_S \frac{\pi D H + 2(\pi D^2/4)}{\pi d^2/4} = 2 P_S \left(2\frac{DH}{d^2} + \frac{D^2}{d^2} \right). \tag{13}$$

Therefore, from equations (12), (13),

$$n_t = \tfrac{3}{2} P_L H \frac{D^2}{d^3} + P_S \left(2\frac{DH}{d^2} + \frac{D^2}{d^2} \right). \tag{14}$$

And the ratio n_s/n_t is

$$\frac{n_s}{n_t} = \frac{2 P_S d \left(\frac{1}{H} + \frac{2}{D} \right)}{\tfrac{3}{2} P_L + P_S d \left(\frac{1}{H} + \frac{2}{D} \right)}. \tag{15}$$

Now from equation (4), the melting temperature of the nanodisc (T_{md}) is derived as follows:

$$\frac{T_{md}}{T_{mb}} = 1 - (1-q) \frac{2 P_S d \left(\frac{1}{H} + \frac{2}{D} \right)}{\tfrac{3}{2} P_L + P_S d \left(\frac{1}{H} + \frac{2}{D} \right)}. \tag{16}$$

2.3. Nanowires ($H \gg D$)

If $H \gg D$, the nanodisc may be called a nanowire and, since $1/H \ll 1/D$, equation (16) for the melting temperature of a nanowire (T_{mw}) reduces to

$$\frac{T_{mw}}{T_{mb}} = 1 - (1 - q)\frac{4P_S\frac{d}{D}}{\frac{3}{2}P_L + 2P_S\frac{d}{D}}. \tag{17}$$

By defining $a = 2P_S d$, $b = 3P_L/2$, $X = 1/D$, the general form of equation for a nanowire is

$$\frac{T_{mw}}{T_{mb}} = 1 - 2(1 - q)\frac{aX}{b + aX}. \tag{18}$$

2.4. Nanofilms ($D \gg H$)

If $D \gg H$, the nanodisc may be considered as a nanofilm and, because $1/D \ll 1/H$, equation (16) becomes

$$\frac{T_{mf}}{T_{mb}} = 1 - (1 - q)\frac{2P_S\frac{d}{H}}{\frac{3}{2}P_L + P_S\frac{d}{H}} \tag{19}$$

where T_{mf} is the melting temperature of the nanofilm. Therefore the general form of T_{mf}/T_{mb} for a nanofilm is

$$\frac{T_{mf}}{T_{mb}} = 1 - 2(1 - q)\frac{aX}{b + aX}, \qquad \text{with } a = P_S d, \quad b = \frac{3}{2}P_L, \quad X = \frac{1}{H}. \tag{20}$$

It is clear that equations (11), (18), (20) have identical form, and this is a general form, applicable for all nanoparticles, nanowires, and nanofilms. In this general form, there is a geometric parameter (q) and, for spherical nanoparticles, nanowires and films, a and b are purely materials constants, depending upon the lattice type and atomic diameter (it is generally assumed that relatively large particles, with $R \geqslant 3$ nm, are spherical [4]). Below we generalize equations (11), (18) and (20) for these three geometries.

2.5. A general equation

By introducing a parameter λ, representing the type of nanosolid ($\lambda = 0$ for spherical nanoparticles, $\lambda = 1$ for nanowires and $\lambda = 2$ for nanofilms), we can write

$$\frac{T_{mn}}{T_{mb}} = 1 - 2(1 - q)\left(\frac{3 - \lambda}{3}\right)\frac{aX}{b + \left(\frac{3-\lambda}{3}\right)aX}, \qquad a = 2P_S d, \quad b = P_L, \quad X = \frac{1}{(\text{size})} \tag{21}$$

where the term $X = 1/(\text{size})$ is the reciprocal of the nanosolid size: $1/D$ for nanoparticles and nanowires (D is the diameter of the nanoparticle or nanowire) and $1/H$ for nanofilms (H is the thickness of the nanofilm).

3. Results and discussion

Equation (21) is a general equation for the size dependence of the melting temperature of nanosolids. We have shown that this general form is applicable to spherical nanoparticles, nanowires and nanofilms if we use the parameter, λ, to represent the type of nanosolid. Applying McLaurin's series to equation (21) gives

$$\frac{T_{mn}}{T_{mb}} = 1 - 2(1 - q)\sum_{k=1}^{\infty}(-1)^{k+1}\left(\left(\frac{3 - \lambda}{3}\right)\frac{a}{b}\right)^k X^k. \tag{22}$$

By using the first and second terms of McLaurin's series, we can extract the following equation:

$$\frac{T_{mn}}{T_{mb}} = 1 - 2(1-q)\left(\frac{3-\lambda}{3}\right)\frac{a}{b}X. \tag{23}$$

And, by replacing the values of a, b from equation (21),

$$\frac{T_{mn}}{T_{mb}} = 1 - 4(1-q)\left(\frac{3-\lambda}{3}\right)\frac{P_S d}{P_L}X. \tag{24}$$

Equation (24) is a linear approximation for calculation of the size-dependent melting temperature of nanoparticles, nanowires and nanofilms.

Using equation (2), the cohesive energy of bulk material with n_t atoms is

$$E_0 = n_t\varepsilon_0 = \tfrac{1}{2}\beta_L n_t\varepsilon$$

where ε_0 is the cohesive energy per atom of the bulk material and ε is the energy of each bond. Therefore, $\varepsilon_0 = \beta_L\varepsilon/2$. Following the model discussed by Qi [22], we may consider that half of the total bonds of each surface atom are dangling bonds, and the contribution of each surface atom to the cohesive energy of the nanosolid will be equal to $\varepsilon_0/2$, so the total surface atom contribution is $n_s\varepsilon_0/2$. The contribution of surface atoms to the cohesive energy is also given as $n_s\beta_S\varepsilon/2$, and therefore

$$\tfrac{1}{2}n_s\beta_S\varepsilon = \tfrac{1}{2}n_s\varepsilon_0 = \tfrac{1}{2}n_s\left(\tfrac{1}{2}\beta_L\varepsilon\right).$$

Hence in the model in [22], in which the effect of lattice and surface packing fraction is not considered (so that $P_S/P_L = 1$), leads to $\beta_S = \beta_L/2$ and $q = \beta_S/\beta_L = 1/2$. Using $q = 1/2$ and $P_S/P_L = 1$ in equation (24), i.e. in our approximation from McLaurin's series, we can derive the following equations.

For nanoparticles ($\lambda = 0$):

$$\frac{T_{mp}}{T_{mb}} = 1 - 4\left(1 - \frac{1}{2}\right)dX = 1 - 2\frac{d}{D}. \tag{25}$$

For nanowires ($\lambda = 1$):

$$\frac{T_{mw}}{T_{mb}} = 1 - \frac{8}{3}\left(1 - \frac{1}{2}\right)dX = 1 - \frac{4}{3}\frac{d}{D}. \tag{26}$$

And, for nanofilms ($\lambda = 2$):

$$\frac{T_{mf}}{T_{mb}} = 1 - \frac{4}{3}\left(1 - \frac{1}{2}\right)dX = 1 - \frac{2}{3}\frac{d}{H}. \tag{27}$$

Equations (25)–(27) correspond to the equations for nanoparticle, nanowire, and nanofilm, respectively, that are reported in [22].

However, the present model (equation (21)) is more general than that derived in [22] (and approximated here). By choosing the parameter q, we can fit the model very closely to experimental data, as illustrated in figures 1–5.

For bulk material, $q = 1/2$, if we assume that surfaces are composed of low surface energy, close-packed crystalline planes. For example, for an fcc lattice, $\beta_S = 6$ and $\beta_L = 12$.

In all of the figures the present model is compared with the liquid drop model [20], which has the general form $T_{mn}/T_{mb} = 1 - A/(\text{size})$. In this model A is a constant depending upon the material and shape of the nanosolid.

Figure 1 shows the melting temperature variation (equation (21)) for In nanoparticles assuming that $q = 1/2$, $q = 1/4$, and $q = 1/8$, illustrating the closest fit with experimental data for $q = 1/8$. In figure 2, for Au nanoparticles, the experimental data are close to the fits
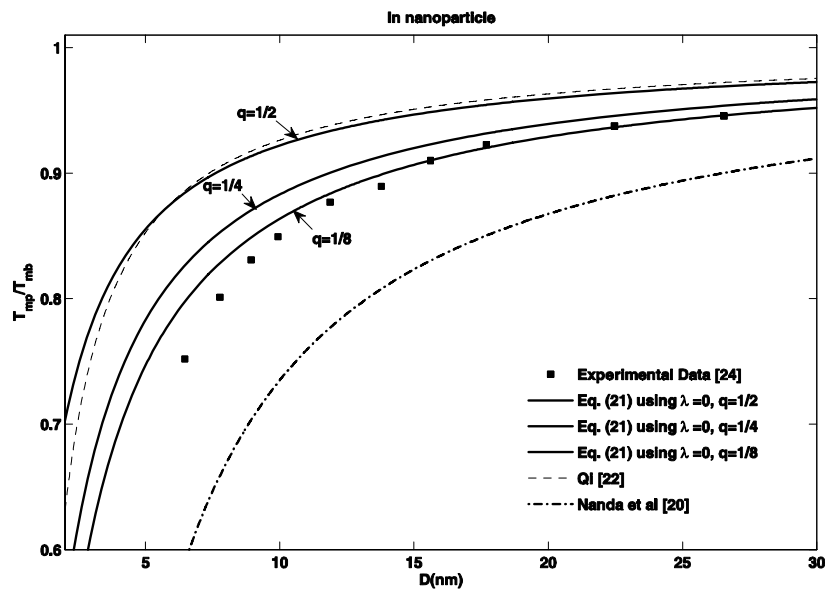
Figure 1. Dependence of melting temperature on the diameter of In nanoparticles. The lattice type of In is body-centred tetragonal (bct) (P_L = 0.68, P_S = 0.78), r = 0.1843 nm and T_{mb} = 429.8 K [20]. Experimental data from [24].
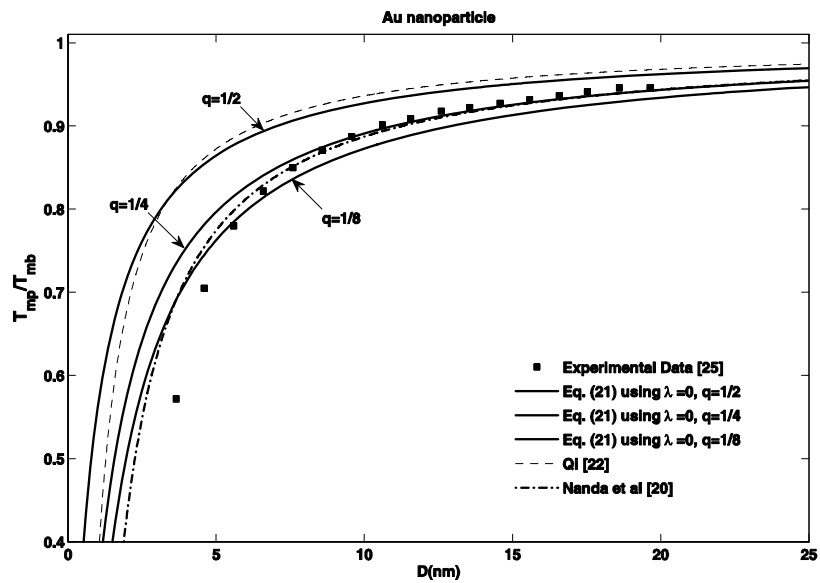

Figure 2. Dependence of melting temperature on the diameter of Au nanoparticles. The lattice type of Au is fcc (P_L = 0.74, P_S = 0.91), r = 0.1594 nm and T_{mb} = 1337.6 K [20]. Experimental data from [25].

for q = 1/4. Also, plots of the liquid drop model [20] are shown in these figures. It can be seen that the liquid drop model is far from the experimental data for In nanoparticles, whilst it shows good agreement with the data for Au nanoparticles.
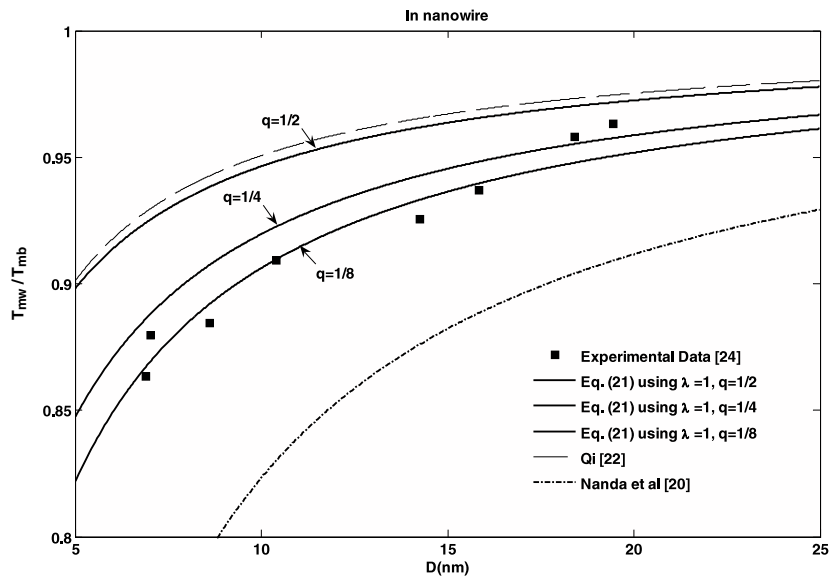
Figure 3. Dependence of melting temperature on the diameter of In nanowire. The lattice type of In is BCT ($P_L = 0.68$, $P_S = 0.78$), $r = 0.1843$ nm and $T_{mb} = 429.8$ K [20]. Experimental data from [24].
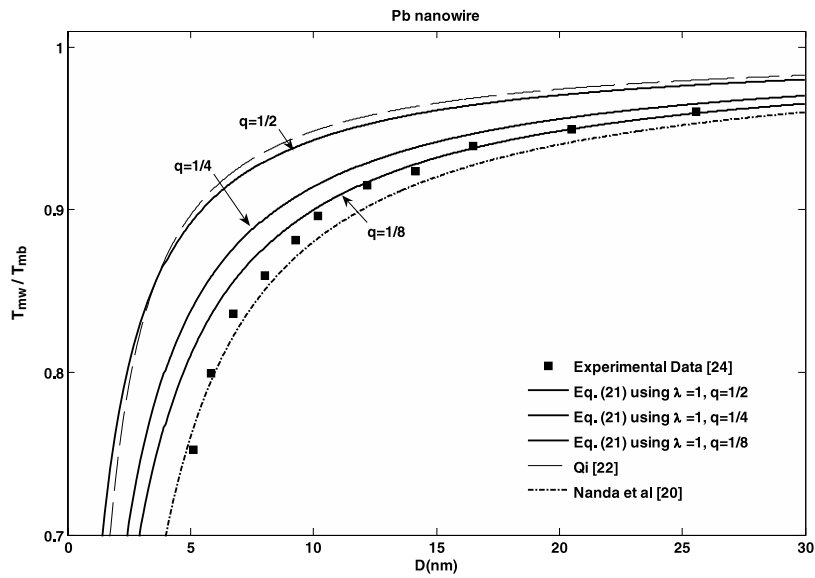

Figure 4. Dependence of melting temperature on the diameter of Pb nanowire. The lattice type of Pb is fcc ($P_L = 0.74$, $P_S = 0.91$), $r = 0.1935$ nm and $T_{mb} = 600.6$ K [20]. Experimental data from [24].

Figures 3 and 4 show similar plots (equation (21)) for In and Pb nanowires, respectively, and figure 5 for a nanofilm of In. In these cases the fit for $q = 1/8$ is closest to the experimental data. The liquid drop model [20] significantly overestimates the reduction of melting point for In nanoparticles, nanowires and nanofilms, but gives a good fit to the data for Pb nanowires.
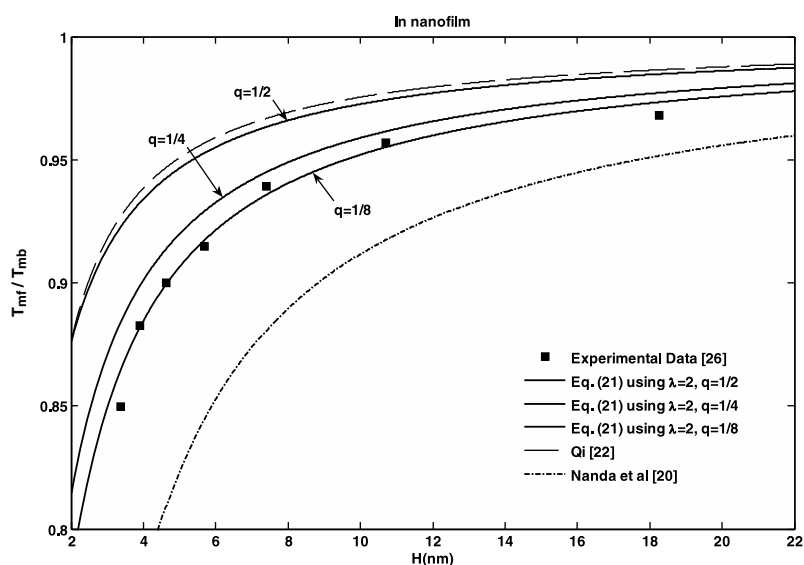
Figure 5. Dependence of melting temperature on the height (thickness) of In nanofilm. The lattice type of In is BCT ($P_L = 0.68$, $P_S = 0.78$), $r = 0.1843$ nm and $T_{mb} = 429.8$ K [20]. Experimental data from [26].

From these figures (figures 1–5) it is clear that the present model can lead to a good fit with experimental data, and that consideration of the packing fractions of the lattice and surfaces of particles leads to a greater predicted reduction in melting temperature with decreasing size than the model of Qi [22]. The total number of atoms in a nanoparticle, as calculated by Qi [22], $n_t = R^3/r^3$, is greater than that in the present model due to the assumption of complete space filling. Therefore, for the same values of q and size, the melting temperature in our model is lower than that of [22].

For nanowires and nanofilms the best fit to our model results from assuming a value of $q = 1/8$, although, if experimental errors are considered, $q = 1/4$ may also give an appropriate fit. Intuitively, by considering the geometry (higher surface curvature), decreasing particle size will lead to more surface dangling bonds and a decrease in the geometric parameter, q. Further measurements of the melting temperature of nanosolids (of different materials, and shapes) will lead to a clearer understanding of the physical meaning of this parameter.

4. Conclusion

An improved model has been developed to account for the melting temperature of nanosolids. In this model the effects of lattice and surface packing fraction, and the coordination number of atoms in the lattice and in the surface crystalline planes, have been included. A general equation for nanosolids (spherical nanoparticles, nanowires, nanofilms) has been derived which includes a parameter, q (the ratio of the coordination number of atoms on the surface to that in the lattice of the nanosolid), which has been adjusted for fitting with experimental data. The model predicts the equations given in [22] and can lead to better consistency with experimental data, as illustrated for nanoparticles of Au and In, nanowires of In and Pb, and nanofilms of In. Our model is also compared with the liquid drop model [20]. Finally the value of $q = 1/8$, 1/4 has been suggested for a geometric parameter to give best fitting for experimental results.

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