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Abstract
The phase diagram of nanoparticles is known to be a function of their size. In the
literature, this is generally demonstrated for cases where their shape is spherical.
Here, it is shown theoretically that the phase diagram of non-spherical particles
may be calculated from the spherical case, at the same surface area/volume
ratio, both with and without surface segregation, provided the surface tension
is considered to be isotropic.

1. Introduction

Particles with a diameter in the range of 1–100 nm are in an intermediate state between the solid
and molecular states. Such particles are characterized by the fact that the ratio of the number
of surface to volume atoms is not small. It is then obvious that the effects of the surface on the
cohesive properties of the particle cannot be neglected. This is seen in various situations, such
as the well known size-dependent melting point depression [1] and other phase transitions [2]
of nanoparticles. Since the surface tension depends on the chemical environment, it is obvious
that the melting point variation also depends on it, as observed experimentally for various
cases [3–5].

Since the theoretical work of Pawlow [6] in 1909, various models have been devised to
describe the variation of the melting temperature with the radius of the particle [7–13] and their
shape [14–16]. Thermodynamical theory is also used to explain how the size and segregation
effects modify the phase diagrams of binary systems [17–20].

Although their shape is often assumed to be spherical-like, there are experimental
situations where other shapes are observed. For instance, upon laser-irradiation of surfaces
in liquids, rods and disc-like nanoparticles are seen [21, 22]. The knowledge of the size and
shape dependence of the phase diagram of nanoparticles is also important for the modelling
of the kinetics of chemical reactions involving nanoparticles. For instance, upon sintering of
nanocrystalline CeO_2 ceramics, the size-dependent melting of the dopant in the neck region
of the particle contacts plays a major role [23].

When dealing with nanoparticles, it is necessary to specify the size range under discussion.
Indeed, in the literature, the term 'nanoparticle' is used for particles having sizes between a

few atoms to so-called 'clusters', up to the 100 nm range. The behaviour of these nanoparticles is different. When the particles contain some hundreds of atoms, their shapes are often well defined polyhedra (see [24] and references therein). Here, we treat cases where the thermodynamical description remains valid, i.e. in the size range above around 3 nm.

In most papers dealing with melting, authors assume that the effect of shape is not important, so that the spherical shape is sufficient to describe how the melting temperature varies. It is the aim of this communication to discuss how geometrical effects may be introduced in the modelling of size- and shape-dependent phase diagrams of nanoparticles. It is shown that these effects are always larger than for spherical particles, owing to the fact that the determining factor is the ratio of the numbers of surface and volume atoms.

2. Theory

The reasoning is based on the calculation of the temperature variation of the isobaric free energy of the liquid phase, $G_l(T)$, relative to that of the crystalline phase, $G_c(T)$, when there is no variation of composition. Let N be the number of atoms in the particle. Since, near the melting point, we are well above the Debye temperature of the solid, the specific heat is approximately constant. Hence, one has:

$$(G_l - G_c)_\infty = C - BT, \tag{1}$$

where C and B are constants for a given material. $(G_l - G_c)_\infty = 0$ at the bulk melting point, $T_{m,inf}$. In the equation, (C/B) is the bulk melting point and C is the latent heat for melting. The subscript ∞ states that we are dealing with very large materials, i.e. the characteristic dimension, R, of the particles is much larger than the interatomic distance. In order to determine how the melting temperature, T_m, varies with R, let us consider relatively large particles (with $R > 3$ nm), where: (i) N is such that the thermodynamical arguments remain valid; (ii) the surface of the particle may be characterized by a single value of the surface tension. At a fixed temperature, the total Gibbs free energy difference for a particle of N atoms is given by:

$$N(G_l - G_c) = N(G_l - G_c)_\infty + fN^{2/3}(\gamma_l - \gamma_c), \tag{2}$$

where f is a geometrical factor depending on the shape of the particle. γ_l and γ_c are the surface tensions of the liquid and the crystal, respectively. In the equation, γ_l and γ_c are related to one atom (i.e. the surface tensions divided by the number of surface atoms). For most inorganic materials, γ remains nearly constant when T varies. Since $(G_l - G_c) = 0$ at T_m, one obtains:

$$T_m = T_{m,inf} + f(\gamma_l - \gamma_c)/BN^{1/3}. \tag{3}$$

The term $(f/N^{1/3})$ is directly proportional to the ratio of surface to volume atoms. For spherical particles, equation (3) may be rewritten as a function of the radius of the particle, R:

$$T_m = T_{m,inf}[1 - \alpha/(2R)]. \tag{4}$$

A careful evaluation of α requires us to also take into account the changes of density on melting.

In the literature, there exist various methods to evaluate α. Some include the surface tensions of the solid and liquid phases explicitly [6–8, 12, 13]. Other models include no adjustable parameter [9, 11]. For inorganic materials in vacuum, α is calculated to be positive, between 0.4 and 3.3 nm.

When the particle is not spherical, the ratio of the surface area, A, to the volume, V, of the particle has to be calculated. Altogether, one may write:

$$T_m = T_{m,inf}[1 - D(f/N^{1/3})] = T_{m,inf}[1 - D(A/V)]. \tag{5}$$

By comparison with the case of the sphere, one deduces that:

$$D = \alpha/6, \tag{6}$$

so that the knowledge of the spherical coefficient is sufficient.

Let us now consider the phase diagrams of binary systems, $A_x B$, with and without surface segregation. In binary systems, the solid–liquid transition is defined by the so-called solidus–liquidus curves. In the case of ideal solutions, the liquidus and solidus curves are calculated from the two simultaneous equations obtained by expressing the equality of the chemical potentials in the two phases [25]:

$$
\begin{aligned}
kT \ln\left(\frac{x_{solidus}}{x_{liquidus}}\right) &= C_A\left(1 - \frac{T}{T_{m,A}}\right) \\
kT \ln\left(\frac{1 - x_{solidus}}{1 - x_{liquidus}}\right) &= C_B\left(1 - \frac{T}{T_{m,B}}\right)
\end{aligned}
\tag{7}
$$

where $x_{solidus}$ and $x_{liquidus}$ define the solidus and liquidus curves at a given T, respectively. $T_{m,A}$ and $T_{m,B}$ are the melting temperatures of elements A and B, respectively. C_A and C_B are the corresponding C coefficients (equation (1)) of elements A and B, respectively.

When the sizes vary and when there is no surface segregation, one has to replace $T_{m,A}$ and $T_{m,B}$ by their size-dependent values (equation (5)) [18]. The same is true for eutectics and regular solutions [19].

When there is surface segregation, things are different, since, at constant global stoichiometry, the 'core' value depends on (A/V) at constant V. Indeed, in our binary system $A_x B$, with N atoms, $Nx/(1+x)$ are atoms A and $N/(1+x)$ are atoms B. Providing the shape does not change with N, the number of atoms at the surface of the particle is equal to:

$$N_s = fN^{2/3}, \tag{8}$$

where f is a geometrical factor, depending on the shape of the particle. At the surface, the composition of the particle is described by $A_{xs}B$. The number of atoms in the 'core' of the particle is then equal to:

$$N_b = N - N_s = N - fN^{2/3}. \tag{9}$$

The composition of the core is described by $A_{xb}B$. The surface segregation is introduced via the segregation energy, E_{segr}:

$$x_s = x_b \exp(E/kT) = Sx_b. \tag{10}$$

Introducing conservation of the number of A and B atoms into the previous equations and assuming that the thickness of the surface is equal to one atomic layer, one obtains:

$$2Sx_b = -(1 + S - R) + [(1 + S - R)^2 + 4Sx]^{1/2}; \tag{11a}$$

$$R = S(1 + x) + fN^{-1/3}(1 - S)(1 + x). \tag{11b}$$

From these equations, it turns out that x_b (i.e. the stoichiometry of the core) and, hence, x_s (i.e. the stoichiometry of the surface) depend on N and x, at fixed T and E, and on the shape of the particle, via the term $(fN^{-1/3})$. This is precisely proportional to the ratio (A/V).

Thus, *the phase diagram of non-spherical particles may be calculated from the spherical case, at the corresponding value of (A/V), both with and without surface segregation, provided the surface tension is isotropic.*

Table 1. Parameter β (equation (13)) for various geometrical shapes.

Shape	β	Remarks
Sphere	4.836	
Cube	6	
Octahedron	5.719	
Icosahedron	5.149	
Spheroids (oblate)	$\pi^{1/3}[3(1-\varepsilon^2)/4]^{2/3}$ $\times \{2(1-\varepsilon^2)^{-1} + \varepsilon^{-1}\ln[(1+\varepsilon)/(1-\varepsilon)]\}$	$\varepsilon = \sqrt{[1-(b/a)^2]}$
Spheroids (prolate)	$(\pi/2)^{1/3}[3/(1-\varepsilon^2)]^{2/3}$ $\times \{(1-\varepsilon^2) + \varepsilon^{-1}(1-\varepsilon^2)^{1/2}\arcsin\varepsilon\}$	$\varepsilon = \sqrt{[1-(b/a)^2]}$
Drop on a flat substrate	$\pi^{1/2}3^{2/3}[2(1-\cos\theta)$ $+ \sin^2\theta]/[2(1-\cos\theta) - \sin^2\theta\cos\theta]^{2/3}$	$\theta = $ contact angle $r = $ radius of the contact surface $R = $ radius of the sphere $h = R(1-\cos\theta); r = R\sin\theta$

3. Discussion

3.1. Geometry

The ratio A/V is calculated by purely geometrical arguments. It is worth noting that, since the sphere is the geometrical figure with the lowest (A/V) at constant V, the size variation of all other shapes is larger than for the sphere. It is interesting to compare various geometries with constant V. Hence, let us explicitly express A/V.

For the sphere:

$$A/V = 3/R = \pi^{1/3}6^{2/3}/V^{1/3} = 4.836/V^{1/3} = \beta \text{ (sphere)}/V^{1/3}. \tag{12}$$

Similarly, for other geometrical shapes, one can express:

$$A/V = \beta \text{ (shape)}/V^{1/3}. \tag{13}$$

A few examples are given in table 1.

3.2. Facetting

The previous reasoning is based on the assumption that the surface tension is 'isotropic'. This is valid for the two following cases. (i) The radius of the particle is relatively large (say, >3 nm) and there is no strong facetting of the solid particle, i.e. it appears 'rounded'. This criterion is met when the particle is synthesized in the liquid phase (as for laser synthesis) and is cooled down. This is obviously not valid for regular polyhedra. (ii) The shape of the particle is a regular polyhedron made of one type of crystal face, since there is only one value of γ_c involved. However, in this case, care has to be taken, owing to the fact that γ_c depends on the crystallographic face, i.e. the factor DA varies from shape to shape as discussed below.

Indeed, in real cases, in the solid state, it is well established that the surface tension is anisotropic; it depends on the crystallographic phase. As seen from equations (2) and (5), the terms determining the variation of the melting temperature with size are the product of the geometrical term (A/V) with the surface tension term $(\gamma_l - \gamma_c)$. In order to evaluate the importance of the latter term, one has to compare its variation with the Miller indexes of the surfaces.

Experimentally, the solid–vapour interface tension, γ_c, is not easily accessible. Semi-empirical theoretical estimates, averaged over different surface orientations have been given for a number of elements [26]. The problem of the estimation of specific interface tensions is more difficult. Variations of surface tensions may reach about 30% between various crystallographic faces. For instance, using a broken bond model, one estimates [27] that, for the face centred

cubic (fcc) lattice, the surface tensions of the (111), (100), (110), (210) faces are in the ratio: 1.00, 1.154, 1.223, 1.275. In this case, one estimates that the total surface 'energies', γA, at constant V, for a cube (with six (100) faces) and an octahedron (with eight (111) faces) are in the ratio 6.924–5.719.

For the evaluation of phase transitions of nanoparticles, the term of interest is not γ_c, but $(\gamma_l - \gamma_c)$. The ratio $(\gamma_c - \gamma_l)/\gamma_l$ is in the 10–30% range for most elements, i.e. the same range as the variation of solid surface tensions between different faces. Therefore, one might expect very strong variations of $(\gamma_c - \gamma_l)$ and, hence, of D (equation (5)) for different crystal orientations and shapes of the nanoparticles. For example, in the case of the fcc nanoparticle, at constant V, the term DA $(=(\gamma_c - \gamma_l)A)$ for the cube is proportional to $6.924 - 6\gamma_l/\gamma_c(111)$. For the octahedron, it is proportional to $5.719 - 5.719\gamma_l/\gamma_c(111)$. When dealing with spheres, the value of γ_c is assumed to be 'averaged over a few crystallographic faces'. Let us assume a 'mean' $\gamma_c = 1.1\gamma_c(111)$. One obtains that, for the sphere, DA is proportional to $5.32 - 4.836\gamma_l/\gamma_c(111)$. Since, for most elements, $\gamma_l/\gamma_c(111)$ is in the 70–90% range, it turns out that the ratio of the values of DA for the octahedron and the sphere varies between 0.89 and 0.59. This implies that the assumption that the surface tension is isotropic has to be discussed carefully when dealing with phase transitions of facetted nanoparticles.

Another limitation of this theory (and others given in the literature) is that there is no premelting (or surface melting). Consequently, one has to introduce the solid–liquid interface energy [28]. However, since the densely packed faces have a lower tendency to premelting than the other faces, one expects that our general conclusion is not affected by neglecting premelting.

References

[1] Buffat Ph and Borel J-P 1976 *Phys. Rev.* A **13** 2287
[2] Damodara Das V and Karunakaran D 1990 *J. Appl. Phys.* **68** 2105
[3] Allen G L, Bayles R A, Gile W W and Jesser W A 1986 *Thin Solid Films* **144** 297
[4] Sheng H W, Xu J, Yu L G, Sun X K, Hu Z Q and Lu K 1996 *J. Mater. Res.* **11** 2841
[5] Radloff C and Halas N J 2001 *Appl. Phys. Lett.* **79** 674
[6] Pawlow P 1909 *Z. Phys. Chem.* **65** 1
[7] Couchman P R and Ryan C L 1978 *Phil. Mag.* A **37** 369
[8] Hoshino K and Shimanura S 1979 *Phil. Mag.* A **40** 137
[9] Wautelet M 1991 *J. Phys. D: Appl. Phys.* **24** 343
[10] Vanfleet R R and Mochel J M 1995 *Surf. Sci.* **341** 40
[11] Zhao M, Zhou X H and Jiang Q 2001 *J. Mater. Res.* **16** 3304
[12] Sun C Q, Tay B K, Zeng X T, Li S, Chen T P, Zhou J, Bal H L and Jiang E Y 2002 *J. Phys.: Condens. Matter* **14** 7781
[13] Nanda K K, Sahu S N and Behera S N 2002 *Phys. Rev.* A **66** 013208
[14] Celestini F and Ten Bosch A 1995 *Phys. Lett.* A **207** 307
[15] Wautelet M 1998 *Phys. Lett.* A **246** 341
[16] Wautelet M 1992 *Nanotechnology* **3** 42
[17] Garvie R C 1965 *J. Phys. Chem.* **69** 1238
[18] Wautelet M, Dauchot J-P and Hecq M 2000 *Nanotechnology* **11** 6
[19] Vallée R, Wautelet M, Dauchot J-P and Hecq M 2001 *Nanotechnology* **12** 68
[20] Wu N-L, Wu T-F and Rusakova I A 2001 *J. Mater. Res.* **16** 666
[21] Link S, Burda C, Nikoobakht B and El-Sayed M A 2000 *J. Phys. Chem.* B **104** 6152
[22] Simakin A V, Voronov V V, Shafeev G A, Brayner R and Bozon-Verduraz F 2003 *Chem. Phys. Lett.* **348** 182
[23] Kleinlogel C and Gauckler L J 2001 *Adv. Mater.* **13** 1081
[24] Yacaman M J, Ascencio J A, Liu H B and Gardea-Torresdey J 2001 *J. Vac. Sci. Technol.* B **19** 1091
[25] Steininger J 1970 *J. Appl. Phys.* **41** 2713
[26] Miedema A R 1978 *Z. Met. Kd.* **69** 287
[27] Regnier P 1978 *Handbook of Surfaces and Interfaces* vol 2, ed L Dobrzynski (New York: Garland)
[28] Pluis B, Frenkel D and van der Veen J F 1990 *Surf. Sci.* **239** 282