

Introduction

This work is concerned with the evaluation of the phase diagrams of nanoparticles and nanowires of different shapes by using the classical thermodynamic theory. To apply that theory, the following hypothesis are required :

- The number of surface to volume atoms ratio is not small.
- The melting temperature of particles decreases with decreasing radius.
- The number of atoms N, must be sufficiently large
- The surface of particles is characterised by the surface tension, γ_s and γ_l
- The theory is valid when the radius of nanoparticle $R \geq 3\text{nm}$.

General theory

The melting temperature of a nanoparticle given by:

$$T = T_{m,\infty} [1 - \alpha/(2R)] = T_{m,\infty} + f(\gamma_l - \gamma_s) / BN^{1/3}$$

$T_{m,\infty}$ is the bulk melting temperature; γ_l and γ_s are the surface tensions of the liquid and the crystal respectively. For inorganic materials α is positive, between 0.4 and 3.3 nm. The term $f/N^{1/3}$ is direct proportional to the ratio of A/V .

Phase diagrams of binary nanoparticles

In the case of ideal solutions, the liquidus and solidus curves are calculated from the two simultaneous equations. These are obtained by expressing the equality of the chemical potentials in the two phases.

$$kT \ln \left(\frac{x_{solidus}}{x_{liquidus}} \right) = \Delta h_{m,1} \left(1 - \frac{T}{T_{m,1}} \right)$$

$$kT \ln \left(\frac{1 - x_{solidus}}{1 - x_{liquidus}} \right) = \Delta h_{m,2} \left(1 - \frac{T}{T_{m,2}} \right)$$

$x_{solidus}$ and $x_{liquidus}$ are respectively the solidus and liquidus curves for a given T. $T_{m,1}$ and $T_{m,2}$ are the melting temperature of elements 1 and 2, respectively, Δh_i is the melting enthalpy of element i.

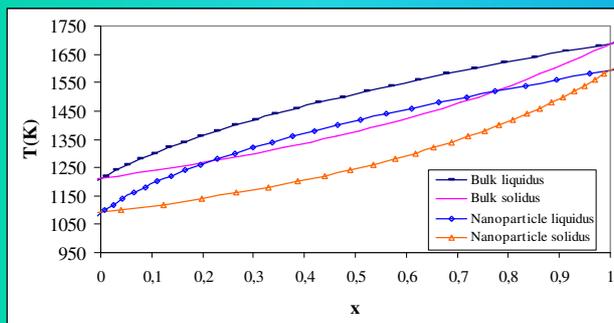


Fig.1 Solidus-Liquidus curves of the system Ge-Si; (top) bulk material, (bottom) spherical nanoparticle (R = 16.8nm)

The influence of shape

When the particle is not spherical, one may write:

$$T_m = T_{m,\infty} [1 - D\beta(\text{shape})/V^{1/3}]$$

the term $D\beta(\text{shape})$ is the shape parameter, V is the volume of the particle. By comparison with the sphere: $D = \alpha/6$

Phase diagrams of binary nanowires

The previous reasoning is extended to the case of nanowires, of section S (with perimeter P) and length L (much larger than: $S^{1/2}$)

$$A=PL \quad V=SL$$

$$(A/V)=(P/S)=\beta(\text{shape})/S^{1/2}$$

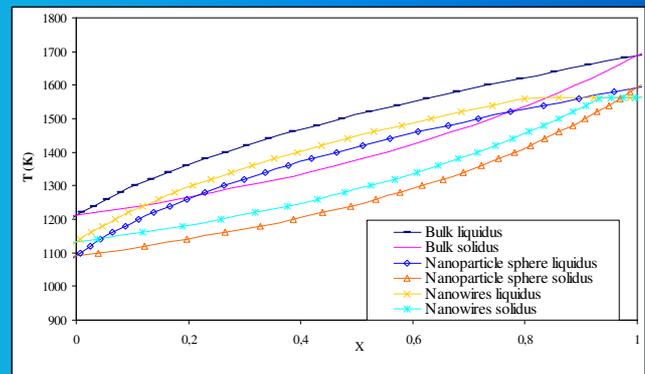


Fig. 2. Solidus-Liquidus curves of the system Ge-Si; (top) bulk material, middle nanowire (R = 16.8nm), (bottom) spherical nanoparticle (R = 16.8nm)

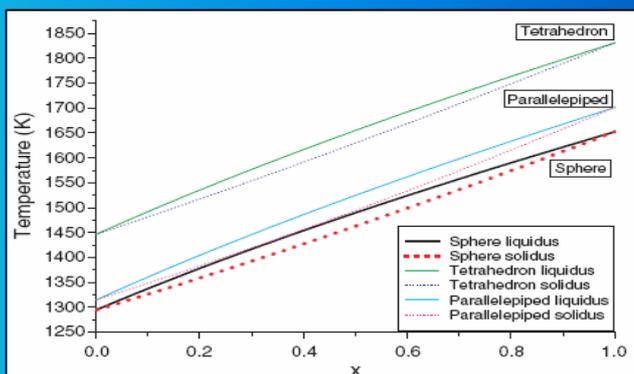


Fig. 3. Solidus-Liquidus curves of the system Cu-Ni nanoparticles of various shapes. From top to bottom: tetrahedron, parallelepiped, sphere.

Conclusion

The phase diagrams of nanoparticles depend on both their size and shape. The model is based on classical thermodynamical arguments under the assumptions that the radius is not too small ($>2-3 \text{ nm}$) and that the concept of surface tension remains valid.

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