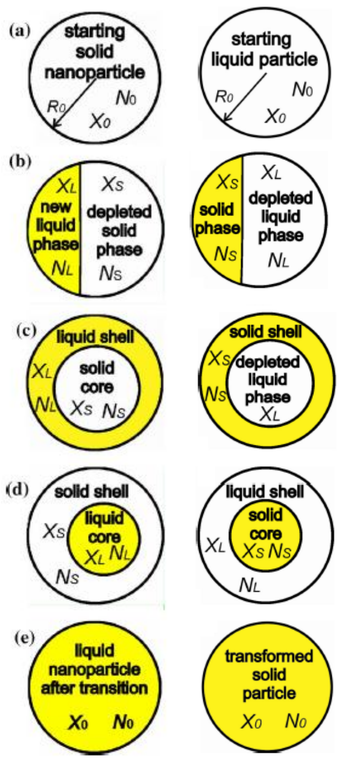
Chemical depletion at Cu-Ni nanophase diagram

Bilogorodskyy Yu.S.
Physical-Chemical Materials Science" Center of the NAS of Ukraine. Kyiv, Ukraine,
Research and Education Institution, "Cherkasy Regional Center of Works with Students, Cherkasy, Ukraine, urabelogorodsky@ukr.net
Shirinyan A.S.
Physical-Chemical Materials Science" Center of the NAS of Ukraine. Kyiv, Ukraine,
aramshirinyan@ukr.net

Introduction

A modified Gibbs thermodynamics to describe the solidification and melting of the liquid Cu-Ni droplet and equilibrium states in two-phase region have been suggested. Such approach [1] takes into account the chemical depletion so that the Gibbs free energy of a changing nanosystem is reassessed as the function of composition, temperature, droplet size and the size of a new phase cluster inside the droplet.

Methodology



A phase change models for different assumptions of the structure of the phases

We consider a start nanoscale system (consisting of Cu and Ni atoms) with stoichiometry X_0 and number of atoms N_0 and assume the formation of a single nucleus of a new phase (of composition X_n and number of atoms N_n) inside.
In general when new phase appears the compositions X_n, X_p and X_0 obey lever rule equation:

$$X_0 \cdot N_0 = X_n \cdot N_n + X_p \cdot N_p,\ N_0 = N_n + N_p$$

For phase transition from single-phase state to two-phase morphology the Gibbs free energy change $\Delta G(X_n, N_n, T)$ has the form:

$$\Delta G = N_0 \cdot g_p(X_0,T) - N_n \cdot g_n(X_n,T) - N_p \cdot g_p(X_p,T) - \sigma_{SL}(X_p, X_n, T) \cdot S_{SL} - \sigma_n(X_n,T) \cdot S_n + \sigma_p(X_0,T) \cdot S_0$$

$N_p \cdot g_1(X_p,T)$ accounts the chemical depletion effect in nano-sized objects and changes the thermodynamics of phase transformation as compared with classical Gibbs theory.

The appearance of a stable minimum of the negative value $\Delta G<0$ for the nonzero value N_n indicates the phase transformation. Additionally, this condition is used as energy minimum criterion.

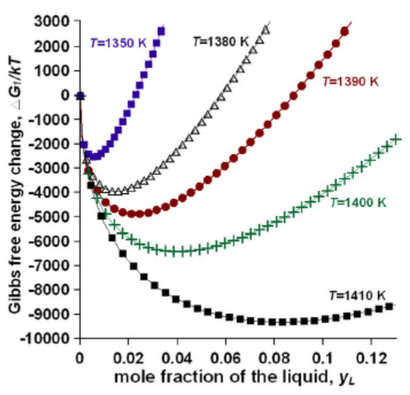
Also we use the often applied condition $\Delta G^*=50kT$ as the nucleation energy barrier criterion.

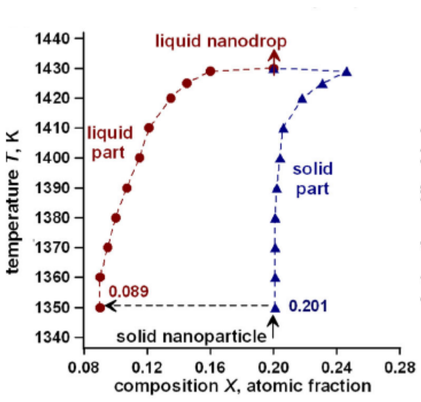
Results

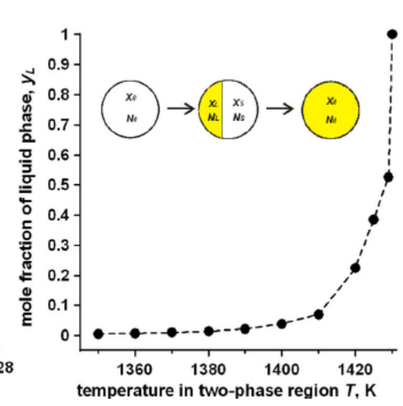
It have been calculated and constructed the phase transformation loops [2, 3] at the size-dependent temperature-composition phase diagram for the isolated Cu-Ni droplet showing a two-phase equilibrium states at 25nm-80nm

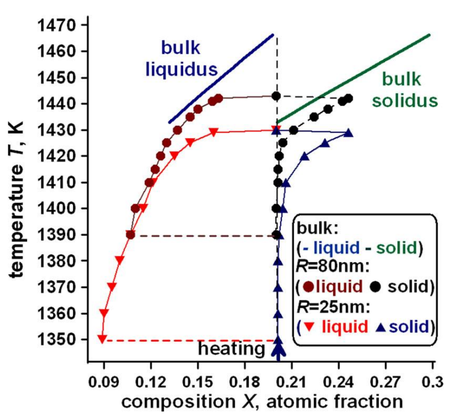
What way begins earlier if we start from a solid nanoparticle?

The dominating mechanism of a solid-to-liquid-phase change in an isolated Cu–Ni nanoparticle is a surface induced melting due to a cap-like configuration (starts at less overheating, less temperatures).



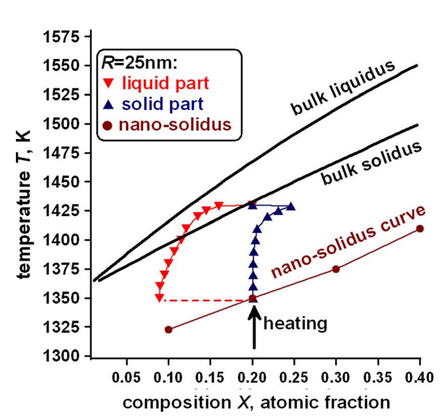






A generalization of the size and depletion effects on the nano-melting loops at the T–X phase diagram of Cu–Ni nanoparticle transforming: three nanomelting loops—for 25 nm (lowest loop, triangles), 80 nm (middle loop, circles) and bulk Cu–Ni system (top loop, solid lines).

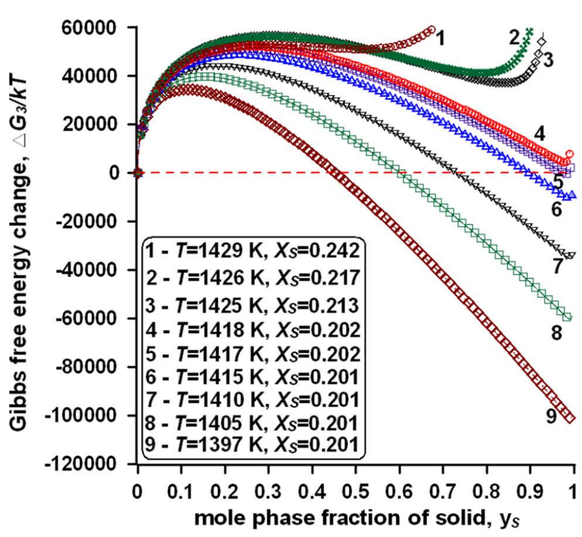
The decrease in the sizes gives the increase in the width of the phase transformation temperature interval.

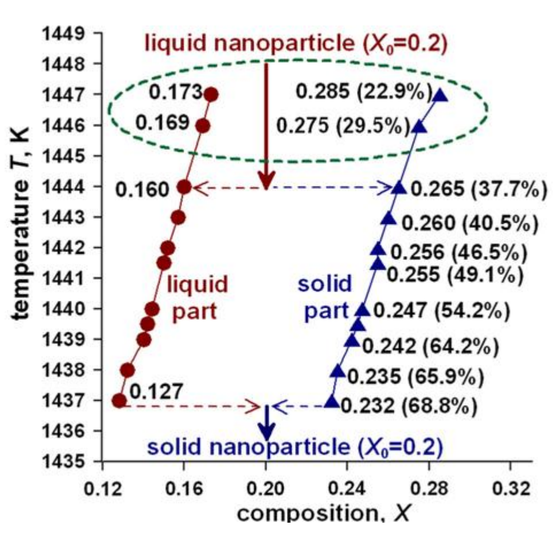


Generalization of the size and chemical depletion effects on the limit solubility curve and nano-melting loops at the T–X diagram of isolated Cu–Ni nanoparticle: two-phase states representing by the nano-melting loop (red and blue triangles) for 25 nm nanoparticle differ from the limit solubility curve and nanosolidus (brown circles) for the same nanoparticle

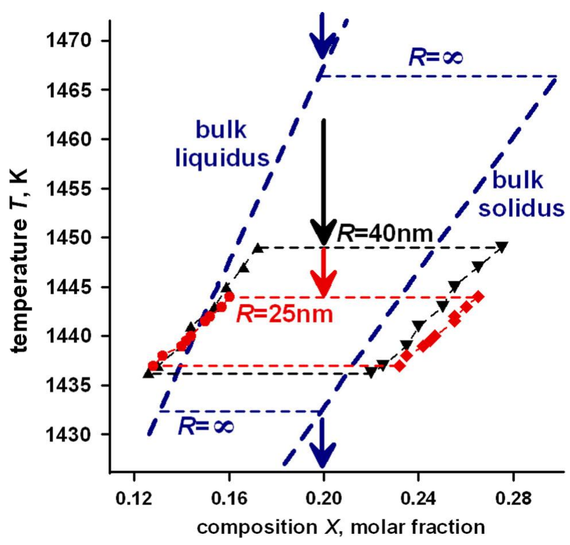
What way begins earlier if we start from a liquid nanoparticle?

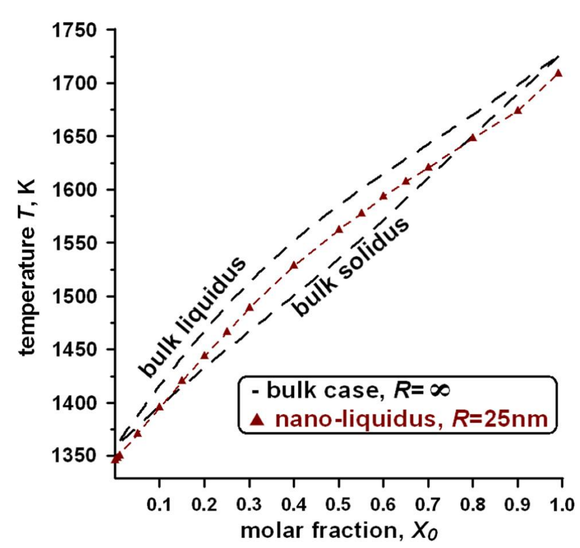
The dominating mechanism of a liquid-to-solid-phase change in an isolated Cu–Ni nanoparticle is a solid core–liquid shell configuration.
The energy barrier for nucleation in the solid core–liquid shell mode is always less than for the phase transition going through a cap-like configuration.





It is interesting that at a low temperature of 1185 K the energy barrier becomes <50 kT and the solidification through a core–shell mechanism may proceed directly without delay and without the existence of two-phase equilibrium states, even without a compositional splitting or a solidification loop.





Generalization of the size and depletion effects on nano-solidification loops in the T–X phase diagram of the Cu–Ni nanoparticle transforming.

When the size decreases, the loop narrows concerning temperatures and broadens concerning compositions and the shape of the loop changes from a trapezoidal to a parallelogram type.

Demonstration of the full macro-phase diagram (dash lines for bulk Cu–Ni system) and solubility curve "nano-liquidus" at R = 25 nm (brown triangles): solubility of Ni increases with decreasing size, the shape of nano-liquidus is changed as compared with bulk liquidus.

Conclusion

- The modification of the Gibbs thermodynamics for multicomponent isolated phase change nanosystems takes into account the finite size and chemical depletion effects and discussed here for the particular case of transforming Cu-Ni nanodrop.
- Results show that the application of the concept of the thermodynamics to closed nanosystems in the case of phase transitions as well as the concept of equilibrium phase diagram have to be revised and one needs a new physically acceptable explanation.
- The most probable morphologies of the phase transition were investigated.
- Nanomelting for a Cu–Ni nanoparticle proceeds most probably from surface segments toward core
- regions when a cap-like solid–liquid configuration gives a phase transition.
- Nanosolidification for an Cu-Ni nanoparticle proceeds most probably from internal segments towards surface regions and solid core – liquid shell configuration has greatest chance to be realized.
- It has been discovered and shown quantitatively that equilibrium loops do not coincide with solubility curves - solidus and liquidus.
- Decreasing the size yields at two-phase region of the phase diagram causes the decrease of the solidification/melting temperature and temperature width of phase transition, the increase of the solubility limit and the concentration width of the tranformation loop, the change of the shape and slope of the equilibrium curves.

References

Shirinyan A, Wautelet M, Belogorodsky Y. Solubility diagram of Cu–Ni nano-system // J Phys Condens Matter.-2006.-**18**. P. 2537–2551
Shirinyan A, Wilde G, Bilogorodskyy Y. Solidification loops in the phase diagram of nanoscale alloy particles: from a specific example towards a general vision // J. Mater. Sci.-2018.-**53**. P. 2859–2879.
Shirinyan A, Wilde G, Bilogorodskyy Y. Melting loops in the phase diagram of individual nanoscale alloy particles: completely miscible Cu–Ni alloys as a model system // J. Mater. Sci.-2020.-**55**. P. 12385–12402