Thermodynamic model for prediction of binary alloy nanoparticle phase diagram including size dependent surface tension effect

Fatemeh Monji, Mohammad Amin Jabbareh*

Department of Materials Engineering, Faculty of Engineering, Hakim Sabzevari University, Sabzevar, Iran

ARTICLE INFO

ABSTRACT

Considering the size effect of nanoparticles on surface tension, a new CALPHAD type thermodynamic model was developed to predict phase diagram of binary alloy nanoparticle systems. In contrast to conventional model, the new model can be applied to the nanoparticles smaller than the critical size (5 NM in radius). For an example, the model applied to Ag − Au binary system and the results were compared with experimental data as well as conventional CALPHAD model and molecular dynamics simulation results.

1. Introduction

Because of their unique properties, alloy nanoparticles have attracted the interest of scientists and industries, especially for use as catalysts [1–5] or nanosolders [6–8]. Due to these applications, the thermal stability of nanoparticles has great importance. Because of the increased surface to volume ration of nanoparticles, the phase stability of nanoparticles is significantly different from those of the bulk materials, for example melting point of the nanoparticles decreased by decreasing particle radius [9,10]. To predict the effect of size on phase stability of alloy nanoparticles, two general approaches are used. The first approach lies on atomistic modeling, including density functional theory (DFT), Monte Carlo (MC) and molecular dynamics (MD) simulations [11,12]. In all cases the knowledge of atomic interactions is required for the simulations. The methods are extremely computer intensive and they are limited to very small nanoparticles (e.g. MD simulations are limited to the particles smaller than approximately 10 nm [13]). The second approaches are based on CALPHAD (Computer Calculation of Phase Diagrams) framework. By adding the surface Gibbs free energy contributions to the total Gibbs energy of the system, Tanaka et al. [14] extended the CALPHAD method for the prediction of the phase diagram of nanoparticles. Later Park and Li [15] suggested a method to calculating phase diagram of nanoparticles with commercial software products. Garzel et al. [13] modified this model further and added the effect of particle shapes in calculations. The model also improved for systems containing intermetallic compounds [16–18] and extended for ternary alloy systems [7]. In comparison with atomistic modeling, the CALPHAD method is much easier to implement but cannot be applied to nanoparticles generally smaller than 5 nm in radius [19]. It should be mentioned that the well known macroscopic thermodynamic laws such as the Second law of thermodynamics may break down for very small systems [20]. Moreover previous studies have found that some thermodynamic properties such as heat capacity and latent heat of phase transformations are size dependent and so changed in nano-scale systems [9,11]. Furthermore it was showed that in very small solid particles lattice parameter [21] and surface tension [22–24] are also changed. Surface energy (or surface tension) is the most important physical quantity, which can explain the identical properties of nanoparticles [9] and also the equilibrium conditions depend strongly on the curvature of the surfaces [25–27].

So, in this work, by considering the size effect of nanoparticles on surface tension, a new CALPHAD type thermodynamic model is developed which can be applied to nanoparticles smaller than critical size (5 nm in radius). The model applied to binary Ag − Au system as an example, and the results compared with the conventional CALPHAD model as well as experimental and MD simulation data from the literature.

2. Thermodynamic model

For an A–B binary alloy system, the total Gibbs energy of a nanoparticle is expressed as [14]:

$$^{\phi}G_{nano} = {}^{\phi}G_{Bulk} + {}^{\phi}G_{Surf} \tag{1}$$

where ϕ denotes the phase of the system, $^{\phi}G_{Bulk}$ is the molar Gibbs energy of the bulk binary alloy and $^{\phi}G_{Surf}$ is the surface free energy contribution.

---

* Correspondence to: Hakim Sabzevari University, Towhid Shahr, P.O.Box: 9617976487, Sabzevar, Iran.
 E-mail address: m.jabbareh@hsu.ac.ir (M.A. Jabbareh).

Table 1

Thermodynamic and physical properties used in the calculation of Ag – Au nanoparticle phase diagram. L denotes liquid and S denotes solid phases. Atomic diameters are taken from Ref [36] and other data from Ref [15].

Variables	Equations
Surface tension	$^L\sigma^\infty_{Ag}(Nm^{-1})=1.207 - 2.28 \times 10^{-4}T$
	$^L\sigma^\infty_{Au}(Nm^{-1})=1.33 - 1.4 \times 10^{-4}T$
	$^S\sigma^\infty_{Ag}(Nm^{-1})=1.675 - 0.47 \times 10^{-3}T$
	$^S\sigma^\infty_{Au}(Nm^{-1})=1.947 - 0.43 \times 10^{-3}T$
Molar volume	$^LV_{Ag}(m^3/mol)=1.0198 \times 10^{-5}+1.1368 \times 10^{-9}T$
	$^LV_{Au}(m^3/mol)=1.02582 \times 10^{-5}+7.797 \times 10^{-10}T$
	$^SV_{Ag}(m^3/mol)=1.12066 \times 10^{-5}$
	$^SV_{Au}(m^3/mol)=1.07109 \times 10^{-5}$
Excess Gibbs energy	$^LG^{Ex,Bulk}_{Ag,Au}(J/mol) = X_{Ag}X_{Au}[-16402 + 1.14T]$
	$^{S(fcc)}G^{Ex,Bulk}_{Ag,Au}(J/mol) = X_{Ag}X_{Au}[-15599]$
Atomic diameter	$h_{Ag}(nm) = 0.32$
	$h_{Au}(nm) = 0.27$

For a non – ideal solution, the molar Gibbs energy of the bulk could be written as:

$$^\phi G_{Bulk} = X_A\,^\phi G^0_A + X_B\,^\phi G^0_B + RT(X_A \ln X_A + X_B \ln X_B) + {^\phi G^{Ex,Bulk}} \tag{2}$$

where $^\phi G^0_A$ and $^\phi G^0_B$ are the standard Gibbs energies of the components A and B in phase ϕ, X_A and X_B are the mole fractions of the components A and B; and R and T are the universal gas constant and absolute temperature, respectively. $^\phi G^{Ex,Bulk}$ is the excess free energy of the bulk in phase ϕ which is usually given by means of the Redlich–Kister polynomials as [28]:

$$^\phi G^{Ex,Bulk} = X_A X_B \sum L_v (X_A - X_B)^v\ (v = 0,\ 1,\ 2,\ \ldots) \tag{3}$$

where L_v is the temperature dependent bulk interaction parameter:

$$L_v = a_v + b_v T + c_v T \ln T + \ldots \tag{4}$$

Where a_v, b_v and c_v are constants.

For isotropic spherical particles the surface Gibbs energy is expressed by Eq. (5) [19].

$$^\phi G_{Surf} = 2C^\phi \sigma^\infty_{AB}\,{^\phi V_{AB}}/r \tag{5}$$

where r is the particle radius, C is the shape factor that is introduced to account the effects of shape, surface strain and the uncertainty of the
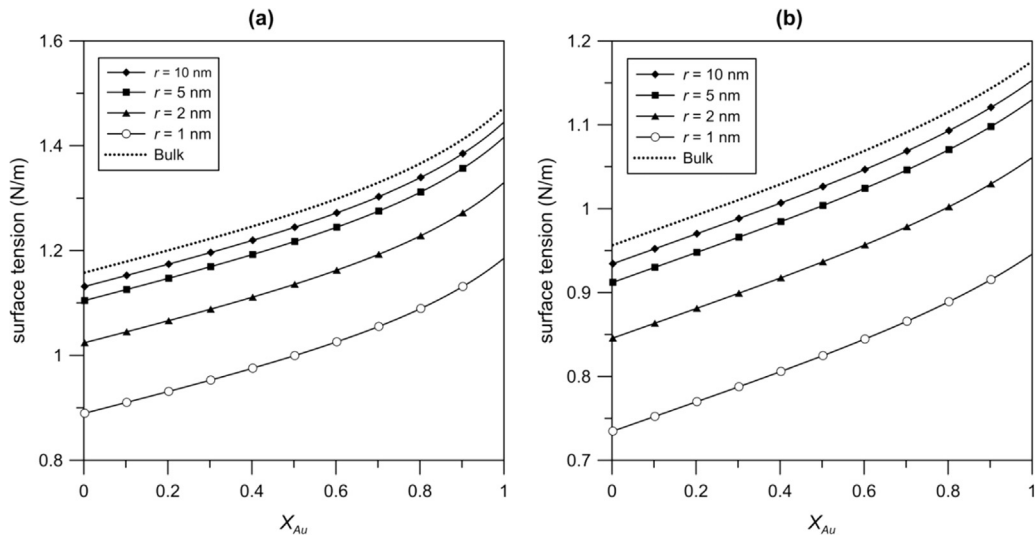

Fig. 1. Concentration dependent surface tension of Ag-Au alloy for solid (a), and liquid (b) phases. Dotted line indicates the surface tension of bulk Ag-Au calculated from Eq. (7).
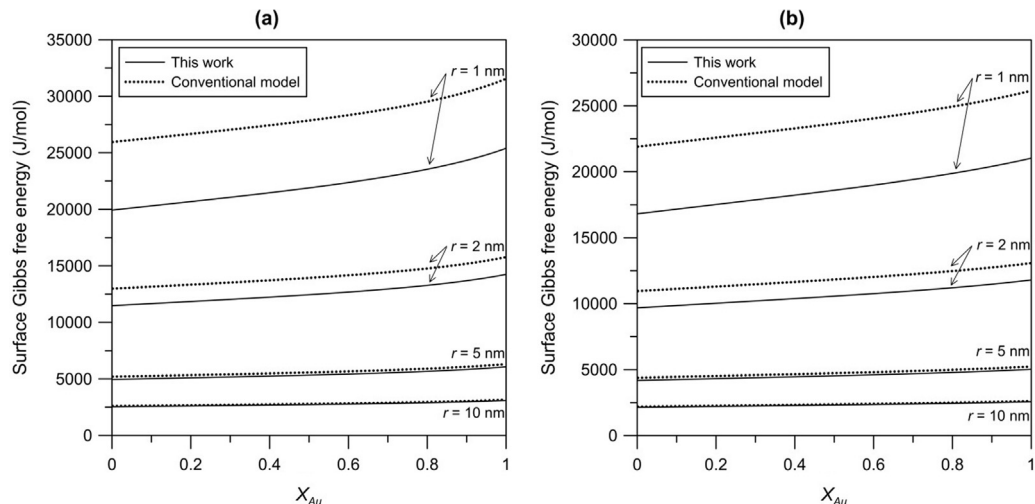

Fig. 2. Calculated surface Gibbs free energy of Ag-Au alloy for nanoparticles with different radius at 1100 K for solid (a), and liquid (b) phases. Solid lines: this work, Eq. (12), Dotted lines: conventional model, Eq. (5).